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CHEMICAL ENGINEERING MATERIALS

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CHEMICAL ENGINEERING OPERATIONS

CHEMICAL ENGINEERING MATERIALS

BY

FRANK RUMFORD

Ph.D.(Glas.), B.Sc.(Lond.), M.I.Chem.E., F.R.I.C.

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PREFACE

THIS book is designed to introduce to students of Chemical Engineering the essential properties and limitations of the materials from which chemical plant must be constructed. The author has noted, through many years, the characteristic gaps in the knowledge of those trained, on the one hand, in mechanical engineering, and, on the other, in chemistry. It is his hope that some of the missing elements may be supplied by this volume. In order to cover both needs, it has been necessary to include much which will be very familiar to the chemist or to the engineer, but not to both.

The material of the plant in which chemicals are handled should ideally be

Unattacked by the chemical reagents used.
Without influence on the chemical process.
Mechanically reliable and easily fabricated.
Essentially economic in cost.

In practice it is rare to find all these desiderata in any single material, and in certain unpleasant processes not one may be completely fulfilled. It is regrettable, also, that no general rules for choice of materials can be laid down. There can be little or no relation between the attack of caustic soda solution on cast iron, and the action of hot reducing gases on silica brick.

The following chapters have been drawn up to show, in the first place, the general mechanism of chemical attack and the essential methods of material testing. The range of materials available is then surveyed, with due regard to relative importance, and the way in which they are usually made up into chemical plant is described. Specific corrosion-resistance data are given and some relative costs suggested. Chemical plant must be primarily designed for corrosion resistance, and only in a secondary degree for strength and economy, as distinct from normal engineering practice. The aim of this work is to provide a survey of chemical plant construction from such a standpoint.

F. R.

Glasgow,
March, 1953

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EXTRACTS from various British Standard Specifications, and references thereto, are given by permission of the British Standards Institution, British Standards House, 2 Park Street, London, W.1, from whom official copies of the Standards can be obtained.

The author is indebted to the Institution of Chemical Engineers and to the Society of Chemical Industry for permission to quote data and to reproduce certain figures. Full references are included in the text.

Due acknowledgement is made in the book to other sources of information, at any rate to the limit of the author's knowledge. With so large a subject to survey, and with data collected over many years, it is more than possible that some worker may be quoted without suitable reference. In such a case the author presents his apologies and hopes that he may be excused. He would like, in any case, to express indebtedness to the works on Corrosion by U. R. Evans and by H. H. Uhlig, and to the "Report on Materials of Construction in the Chemical Industry", published by the Society of Chemical Industry. All three are referred to often in the text of the present book.

ABBREVIATIONS

In references to journals the author has tried to follow the conventions laid down for British Abstracts. Books are cited originally by full title and publishing date, and afterwards by author's name and book title. The "Report on Materials of Construction" referred to above is abbreviated to "Materials of Construction".

Temperature figures throughout the text are given in *Degrees Centigrade* unless specifically stated in other terms. It is appreciated that this may present some difficulty to those who are more used to a Fahrenheit scale, but the author feels that the balance of advantage is on the side of Centigrade units.

CHAPTER 1

THE MECHANISM OF CORROSION

Corrosion may be defined as chemical reaction between the constructional material of a chemical plant and the chemicals with which it is in contact. As such, the reaction will follow normal rules, with rates of attack varying according to temperature and concentration in the reaction zones. In the most common case of corrosion—the rusting of iron and its alloys in contact with air and water—enormous amounts of damage can be traced to the action of these very mild reagents. The annual cost of protection, by paint or similar means, has been estimated[1] at two hundred million pounds sterling in Great Britain alone. Yet the iron still rusts, and the wastage of metal must cost the community as much again, quite apart from the consequences of a fall in operating efficiency caused by structural weakening or corrosion by-products. If this is the case in ordinary surroundings, the problem becomes infinitely more serious when chemical plant is to be built, and a wrong choice of material might lead to complete destruction of a valuable operating unit in a matter of hours. Obviously, then, the first and most outstanding quality in a chemical engineering material must be its resistance to chemical attack.

All corrosion reactions are of heterogeneous surface type, at any rate in their initial stages. In the case of a metal going into solution in an ionising solvent, the surface atoms pass from the solid structure and form positive ions, while the metal surface acquires a corresponding negative charge relative to the solution. Were it possible to prepare a perfectly homogeneous metal surface, entirely in contact with the solvent, reaction would presumably be brought to a complete stop by these opposing electrical forces. It is universally true that the surface is not homogeneous, and in these circumstances certain areas will not be so strongly charged as the others. Current will flow through the metal and the solution, and the negative charges react with hydrogen ions to form free atoms. When these can be freely discharged, reaction proceeds steadily, with the metal dissolving at one point, while hydrogen is evolved at another. This can easily be observed in the dissolution of ordinary commercial zinc in dilute hydrochloric acid. Atoms lose electrons at the solution point, a form of oxidation, while at the hydrogen liberating areas electrons are gained, a reduction process. The seat of corrosion becomes an oxidation–reduction cell with anodic and cathodic areas, and reaction rates governed by electrolytic solution potentials.

These potentials represent the tendency for a metal to pass into solution, acting as an anode in the cell. They will clearly vary with the concentration of metallic ions already present in solution, but are normally measured with a standard concentration of one gram ion per litre. Table I–1 sets out the electrode potentials of the more common ions measured in this way (at 25° C.).

TABLE I–1

Atom	Ion	Volts	Atom	Ion	Volts
K	K^+	−2·922	H_2 (1 atm.)	H^+	0·0
Ca	Ca^+	−2·840	Cu	Cu^{++}	+0·345
Mg	Mg^{++}	−2·380	O_2 (1 atm.)	OH^-	+0·401
Al	Al^{+++}	−1·670	Cu	Cu^+	+0·522
Zn	Zn^{++}	−0·762	Ag	Ag^+	+0·799
Fe	Fe^{++}	−0·440	Pt	Pt^{++}	+1·200
Ni	Ni^{++}	−0·230	Cl_2 (1 atm.)	Cl^-	+1·358
Pb	Pb^{++}	−0·126	Au	Au^{+++}	+1·420

These values show to what extent the potential of a metal, or gas-saturated electrode, would rise in order to check further formation of ions when in contact with a solution of standard concentration. It will be appreciated that all these potentials are relative, and have been arbitrarily assessed against a standard zero potential given by the hydrogen electrode. (This is made up from a platinum-black surface, around which hydrogen gas at 1 atm. pressure is bubbled, immersed in an acid solution of normal hydrogen-ion concentration.)

If two dissimilar metals are immersed in a conducting solution and electrically connected externally, then one, the anode, will tend to pass into solution, while the cathodic partner will receive positive ions in equivalent amount from the solution. In an ideal "reversible" cell, each metal is immersed in a solution of its own salts, thus

Metal A/Salt of A in solution/Diaphragm/Salt of B in solution/Metal B

The total cell potential causing reaction is then made up from the algebraic sum of the two separate electrode potentials, or the two "half-cell" potentials. Then the normal electrode potentials set out in Table 1 are given by a metallic half-cell balanced against a standard hydrogen electrode. Thus a cell made up from iron in contact with a normal solution of ferrous ions and a hydrogen half-cell will develop a potential of 0·44 volts. As current flows, the amount of iron in solution, and consequently the concentration of ferrous ions, will increase. The potential of the cell will diminish as a result, and the complete formula for the potential of an iron electrode can be written as

$$\text{Fe/Fe}^{++}-0{\cdot}440 \text{ v.}+(0{\cdot}030 \log_{10} C)\text{v.}$$

where the effective concentration of ferrous ions is C times the normal value. The constant 0·030 is for a divalent ion; for monovalent ions this is altered to 0·059, and for trivalent to 0·020.

In many metallic half-cells, initial solution gives a steady increase in concentration, with corresponding decrease in potential, until the limits of solubility of some compound of the metal are reached. Then this compound will separate as a solid, and any further dissolution of the metal will produce more precipitate, with no effect on the potential, provided that the solid does not interfere with the electrode surface proper. A cell of this kind, with the metal being steadily converted to some insoluble form, usually an oxide, is the most common basis of continued corrosion. The steadiness of the potential is shown by the use of such systems as standard "half-cells" in the measurement of electrode potentials. The Calomel Electrode is made up from mercury in contact with N/1 potassium chloride saturated with mercurous chloride (calomel); it has an electrode potential of +0·281 volts at 25° C., and is generally used as a convenient substitute for a hydrogen half-cell.

When two identical electrodes are immersed in a suitable ionising solution, no e.m.f. will be generated between them. An external voltage applied to the cell will cause solution of metal at the induced anode and corresponding deposition at the induced cathode. The voltage necessary to cause this action should be very small, though rising slightly, even in stirred solutions, by reason of concentration changes in the regions immediately adjacent to the electrodes. In fact, a much greater increase in voltage is required, owing to the development of an "overpotential". This increase in the apparent resistance of a cell is due to specific changes in the surface condition of the electrodes, which are said to be "polarised". The overpotential characteristics of any material are quite specific, and bound up in the actual atomic structure. Silver gives practically no overpotential, but the effect is very marked with iron and ferrous alloys. A resistance of this kind to the liberation of atoms at an electrode surface must diminish the effective driving force causing electrolytic action and corrosion.

The most important overpotential is that involved in the release of hydrogen, as the molecule H_2, from an electrode. The initial formation of atomic hydrogen at a cathode, followed by association of two atoms to give the molecular form, will follow the two stages

$$(1)\quad H_3O^+ + e \rightarrow H + H_2O, \qquad (2)\quad H + H \rightarrow H_2$$

The e.m.f. required to bring these about varies widely (*a*) with the material from which the cathode is constructed, (*b*) with the current density. A general equation may be written as

$$\text{Overpotential} = \alpha + \beta \log \text{(Current Density)}$$

where α and β are constants for the cathode material.

Precise reasons for this effect have not been established. Either of the steps (1) and (2) above could be responsible for the checking of hydrogen discharge. The second—association of atomic hydrogen to form the molecule—is perhaps more intimately associated with the actual surface condition of the electrode. As it is known that the surface exercises a marked effect on overpotential, the bulk of resistance to hydrogen discharge is probably due to the slow association of hydrogen atoms. These accumulate at the solid surface, and are discharged at a rate which is proportional to the catalytic properties of the electrode for this type of atomic association. At very high current densities, the surface will always be completely covered by an atomic hydrogen film, and a tendency may appear for fresh H^+ ions to combine directly with adsorbed H atoms and electrons to form molecular hydrogen

$$H^+ + H + e \rightarrow H_2$$

The overpotential, on this basis, will increase steadily with current density up to a ceiling figure, and will then remain constant whatever the further increase in density. According to Hickling and Salt[2] high adsorptive and catalytic powers (in, e.g., platinum black) are associated with low hydrogen overpotential, while metals such as tin and lead, with negligible catalytic powers, show high values for the overpotential. The actual voltage levels required to liberate hydrogen at certain surfaces are shown in Table 2.

TABLE I–2[3]

Material	Potential required to liberate Hydrogen Gas at a Current Density of	
	1 amp/sq. dm.	10 amps/sq. dm.
Lead	1·09	1·18
Tin	1·08	1·22
Aluminium	0·83	1·00
Graphite	0·78	0·98
Silver	0·76	0·88
Nickel	0·75	1·05
Zinc	0·75	1·06
Copper	0·58	0·85
Iron	0·56	0·82
Gold	0·39	0·59
Polished Platinum	0·07	0·29
Platinum Black	0·03	0·04

When these overvoltage effects are compared with the electrolytic solution pressures one reason is suggested for the very slow action of acids on such metals as tin and lead. These have normal potentials of —0·136 and —0·126 volts respectively. The potential difference between anodic and cathodic patches can only be small, even in strong acid solutions, and current flow will be stifled by the very high voltage required for hydrogen liberation. If oxygen or oxidising agents are present, then the hydrogen layer causing polarisation may be destroyed. Alternatively certain active elements or "poisons" can act in the reverse direction and check the formation of hydrogen gas. Arsenic, well known for selective action on catalysts, is also one of the most potent agents for this inhibition of hydrogen liberation. When present in the electrolyte of a cell with an iron cathode, the arsenic forces the hydrogen into and through the metal, while very considerable overvoltage effects are noted.

It has already been indicated that the precipitation of some sparingly soluble compound may fix the ionic concentration of a metal at one definite level. If this precipitate is deposited as a compact continuous layer immediately adjacent to the metal surface it will interfere with the smooth flow of ions, giving an increase in the internal resistance of the electrolytic corrosion cell. In the system

Metal A/Solution/Metal B

a potential is set up by anodic action at metal surface A and cathodic action at surface B. Now, if metal A forms an insoluble skin by reaction with the electrolyte in the early stages of corrosion a secondary electrode will be introduced

Metal A/Compound AO/Solution/Metal B

The total potential developed between surface A and surface B must still be the same, but the bulk of this voltage may now be required to force ions through a skin formed by compound AO. The potential drop from the exposed side of the skin to surface B may be negligible and the current passing, a measure of the reaction rate, will be equally small. In an electrolytic cell with an external source of current, the formation of an adherent skin of this type will give the same polarising effect as the concentration of atomic hydrogen on the cathode surface. The film may only have an apparent existence while the external e.m.f. is applied, and may be looked upon as adsorbed atomic oxygen. The liberation of oxygen as a gas does call for a very considerable overvoltage, even at a platinum surface. As a rule, however, an oxide film is definitely formed at the anode, and with many metals can show a very considerable resistance to the passage of current.

The simple electrolytic cell which is set up in most corrosive conditions consists of two differing metallic surfaces, connected electrically by a metal path of negligible resistance, and in contact with a conducting solution. A potential difference is set up, and the anodic metal starts to dissolve at a rate proportional to the current passing. Now the initial current may be proportional to the static equilibrium potentials of the two half-cells concerned, but almost immediately the secondary effects noted above come into play and the reaction rate diminishes. Consider the cell made up from metallic iron and graphite which is invariably formed on a moistened cast-iron surface. If the moistening liquid is an iron-free neutral water, the original potential of the half-cell Fe/H_2O will be very large, but will drop almost immediately to a steady figure corresponding to the limiting concentration of $Fe(OH)_2$ in solution. The graphite will give no ionisable form, and the cathodic reaction will be the discharge of hydrogen ions, followed by hydrogen liberation. As the solution is neutral, the concentration of H^+ ions is 10^{-7} times the normal activity. In these circumstances the complete corrosion cell may be represented as

$$Fe \rightarrow Fe^{++} - 0{\cdot}463 \text{ v.}/2H^+ \rightarrow H_2 - 0{\cdot}414 \text{ v.}$$

and it follows that the total e.m.f. causing reaction is —0·049 volts. With such a small net driving force, overvoltage effects at the electrodes will reduce the current passing, and hence the corrosion, to a very small figure. It will be anticipated therefore that neutral air-free water will have little or no action on the iron–carbon couple.

If the cathodic area is freely aerated, oxygen passes into solution, and the following reaction can take the place of hydrogen liberation

$$O_2+2H_2O+4e \rightarrow 4(OH)^- + 0{\cdot}814 \text{ v.}$$

The complete cell reaction

$$2Fe+2H_2O+O_2 \rightarrow 2Fe(OH)_2$$

has a total driving force of —1·277 volts, with no production of hydrogen gas and no consequent overvoltage troubles. Reaction can be rapid, with iron dissolving at the cathode and being subsequently precipitated as ferrous hydroxide, or further oxidised to ferric hydroxide by more dissolved oxygen.

The very large change in corrosion potential is due to the depolarisation of the cathode by oxygen. The results are so marked that even if the carbon had not been present to serve as a natural cathode, some unaerated section of the surface might have served as a focal point for attack. Over the rest of the metal, the presence of oxygen would lead to the rapid discharge of electrons and the formation of areas cathodic to the unaerated section. Metal would pass steadily into solution to redress the balance, and reprecipitate as the hydroxide. On the other hand, oxygen tends to spread all over the surface and form an oxide film, while the slightly soluble ferrous hydroxide takes up oxygen, in solution, to form much less soluble compounds. If the whole solution is rich in oxygen, this last action occurs almost as soon as the ferrous ions appear, and a coherent film of corrosion product over the whole anodic area checks further action. Oxygen, in fact, always tends to decrease overvoltage effects at the cathode, and to increase similar effects at the anode.

In any chemical plant built up from metals, in contact with ionising solutions and air, a multitude of electrolytic cells will be set up, and any of these which produce a soluble anodic product, combined with rapid oxygen supply to the cathode, will set up marked corrosion. It may be that the reactions involved will be sufficiently effective to cause hydrogen discharge, or that other oxidising agents will replace the oxygen, when attack will be equally rapid. The main factors in checking this corrosion will be the changes at electrodes produced by polarisation or overvoltage. Operating conditions in these cells can be represented by Fig. I-1, in which *A—B* is the initial effective e.m.f., falling as current flows until a steady value *a—b* balancing the final electrical resistance of the cell is reached. The measure of the steady current given by this e.m.f. represents the final corrosion rate, as determined by the normal laws of electrolysis. The fall in e.m.f. can be due to both cathodic and anodic effects, as shown in Fig. I-2. In the first case (2*a*) the changes are most marked at the cathode, while in (2*b*) falling off is mainly at the anode. These two forms are defined as (2*a*) Corrosion under Cathodic Control, and (2*b*) Corrosion under Anodic Control.

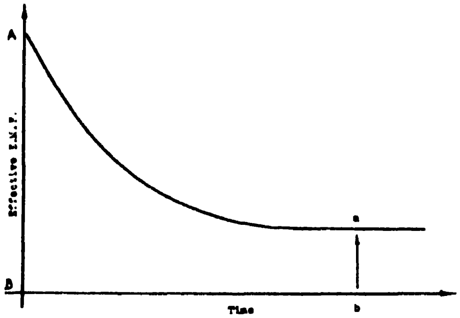


Fig. I-1.

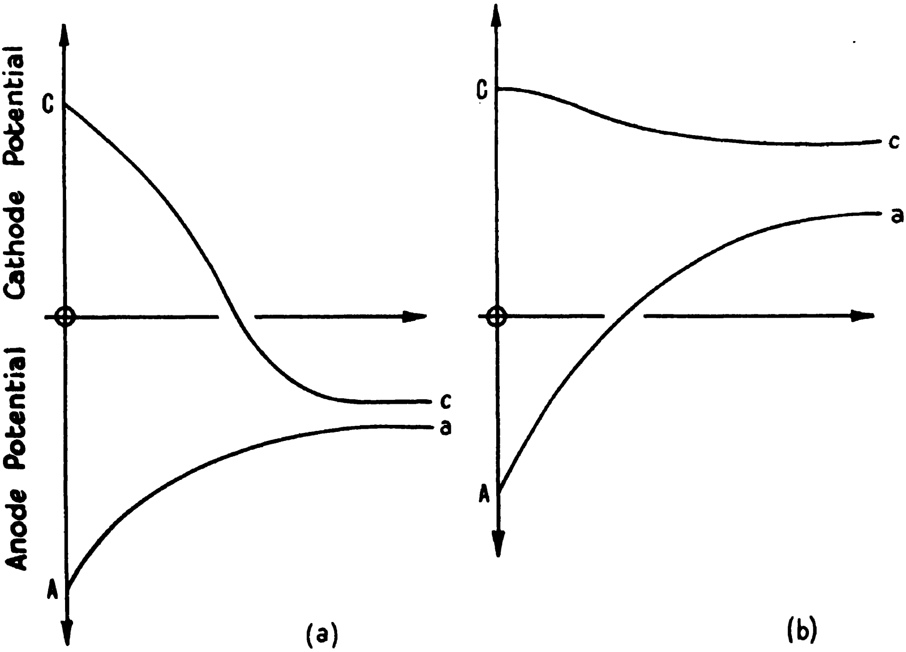


Fig. I-2.

When a mild-steel tank is partly filled with water and left exposed to the atmosphere, rusting goes on fairly evenly over the submerged metal, with an area just round the water-line almost unattacked. This is the section which is cathodic to the rest of the metal by virtue of better aeration, and the rate of attack over the corroded sections is finally determined by the rate of oxygen supply through the upper water layers to the cathodic area. Then the degree of overpotential at the cathode determines the corrosion rate, and the reaction is clearly under cathodic control.

Aluminium metal, freshly prepared in an oxygen-free atmosphere, is attacked rapidly by boiling distilled water, liberating hydrogen freely at points which are slightly cathodic to the rest of the surface. The reaction falls off very rapidly in rate, and is almost imperceptible at the end of thirty minutes. This is due to the formation of a layer of aluminium hydroxide covering the entire surface of the metal, and sealing off cathodic and anodic areas alike. Even if a stable cathodic area exists, or a two-metal couple is formed, transport of ions through the hydroxide is so slow that the original high anodic potential is reduced to a very small effective figure. Corrosion is completely under anodic control.

When these natural protective changes can be enhanced, or circumstances avoided in which they can be checked, corrosion will necessarily be reduced. In the final analysis of an oxidation–reduction cell, it is hydrogen which gives the protective cathode covering, while at the anode migration of the metal ions into solution will be checked by any continuous membrane. The most natural anodic membrane is formed by the oxide or hydroxide of the metal, but any other covering will serve, provided that it is sparingly permeable to ions and *continuous*. A decrease in the overall rate of corrosion is not nearly so important as the checking of localised attack. Very few reaction vessels dissolve completely away, but many are holed and rendered useless by a local concentrated attack. A very important distinction can be made between substances which tend to reinforce cathodic protection—cathodic inhibitors—and those which decrease the effective anode potential—anodic inhibitors. In the first case, irregular application of the inhibitor is of no importance; the area for hydrogen discharge grows smaller, and the natural overvoltage grows with increase in current density. Irregular application of an anodic inhibitor leaves areas in which the rate of solution of the metal may be actually increased, as all the surrounding inhibited areas have become cathodic. Intense local corrosion produces pitting and finally perforation. A typical example of this localised failure is found in the action of sea water on stainless steel. The alloy resists attack by virtue of a complex oxide skin, and is normally quite immune from salt-water corrosion. The metal has no toxic effect on marine organisations or even shellfish, which can grow on local sites and create an unaerated area. Then a differential aeration cell is set up, in which penetration of the metal at rates as high as 1 inch a year can occur. The phenomenon of "stress corrosion", or rapid local attack on metal which has been put under stress, is due in all probability to the failure of a protective anodic film and the creation of a local anodic area. Anodic inhibitors are therefore classed as dangerous, with irregular or insufficient use promoting the formation of small anodic and large surrounding cathodic areas. Cathodic inhibitors, which cannot localise anodic attack, are always safe, but unfortunately much less permanent than their opposites.

CATHODIC INHIBITION

As the characteristic cathode reaction is the discharge of hydrogen, either by oxidation or as free gas, any film which checks the movement of hydrogen ions or of dissolved oxygen towards the cathode will diminish corrosion. Now the characteristic cathodic reaction

$$H_2O+O+2e\rightarrow 2OH^-$$

will increase the local OH^- concentration, creating an alkaline zone. If salts are present in solution which are sparingly soluble in basic conditions, they will tend to precipitate and blanket the cathode. Calcium and magnesium salts in neutral waters will give an initial precipitate of carbonate or hydroxide, which may later react with the metal to give a complex deposit. Whatever the final form, there appears little doubt that the relatively slow attack of "hard" natural waters on many metals is due to a cathodic inhibition of this kind. Acid conditions in the body of the solution will diminish the local alkalinity and check precipitation. An excess of carbon dioxide over the amount required to form bicarbonates will act in this way with lime-bearing waters. The excess has been termed "aggressive carbonic acid", and can be removed by the addition of free alkali. If this addition is overdone, then the calcium salts are thrown down completely, as in water-softening, and the inhibiting properties of the natural water are destroyed. It is well known that many softened waters are much more corrosive than the original untreated water, and the tendency of water to give an inhibiting film of $CaCO_3$ has been expressed by a "saturation index".[4]

The carbonate film appears to be stabilised by traces of phosphate and is no longer so sensitive to carbon dioxide concentration. Raistrick[5] attributes this to the adsorption of an O–P–O–P– complex on the calcite crystal structure, which is thereby inhibited from further growth or solution. The action is definitely confined to the cathode, as shown by the effect of cleaning electrodes in a "two-metal" cell after the carbonate-phosphate film had formed. Scouring of the anode gave no change, but cleaning of the cathode immediately increased corrosion currents to their initial value.

The action of these carbonate precipitates is clear enough, but many other cathodic inhibitors can hardly function in this way. Arsenic has already been mentioned as checking the discharge of hydrogen, while sulphur and mercury derivatives seem to act in the same way. As a result cathodic overpotential is increased, and hydrogen-evolving corrosion is checked. The addition of 0·003% of butyl sulphide to a 5% H_2SO_4 solution cuts the corrosion rate on mild steel by 90%. A direct connection between hydrogen overpotential and corrosion rate has been traced by Chappell *et al.*[6] in the case of quinoline ethiodide, a basic inhibitor used in steel pickling (see p. 108). A number of colloids of the type of starch or glue will also check the attack of acid solutions on metal or the general corrosion by aerated water. The colloidal molecules generally carry a positive charge in acid solution, and may be attracted to the negative cathodic areas, orienting themselves to cover active points. Alternatively, a semipermeable membrane can be formed over the entire metal surface, pinned down in spots by adsorption, and checking all forms of ionic diffusion. In this case, of course, the colloid is not acting specifically as a cathodic inhibitor, but it will blanket cathode and anode alike, avoiding the danger of localised attack caused by many anodic agents.

When oxygen is present to depolarise the cathode, hydrogen overvoltage becomes less important, but some metal surfaces are more effective in bringing about depolarisation than others. Copper is much more active than stainless steel, and will give twice the steady corrosion current of the latter when coupled to a zinc anode in freely aerated NaCl solution.[7]

The great advantage of any cathodic inhibitor is that a local shortage does not cause pitting and subsequent perforation. It is always safe to add such inhibitors, even when the essential reaction is under anodic control, a point made at length by Evans.[8] Unfortunately, these cathodic agents are not, as a rule, firmly attached to the metal. A reactive surface cannot be given some form of protective film, and then used for a variety of reagents, as is so often the case with anodic inhibition.

ANODIC INHIBITION

As any fault in such an inhibitor will give rapid local action, it is essential that the covering shall be continuous, as well as tough enough to resist fracture by localised stress. The most natural agent is some oxidised form of the metal below, formed *in situ*, and growing to cover the whole of the active surface. This means that the oxide must be greater in volume than the metal, when growth will take place under pressure, and a few molecules of thickness will form a complete screen. Fortunately, this is generally true of metals, with the exception of the alkali or alkaline-earth groups. There is no doubt of the existence of such films, and many workers have shown how to detach them from the metal and study their structure at convenience. The most common reagent employed is now a solution of iodine in anhydrous methyl alcohol,[9] but an electrolytic method recently described by Evans and Tomlinson [10] may have some advantages.

Corrosive attack on metal which has formed an oxide film can proceed either by passage of the metal ions through the skin, diffusion of active ions inwards, or by a "peeling off" of the oxide. The first is probably the most common in atmospheric corrosion: migrating electrons are taken up by moist oxygen layers to form OH^- ions, and these combine with the metallic ions to form more hydroxide. The film grows steadily in thickness from the outside surface. Conducting properties vary widely, and may be selectively better for one constituent of a metal mixture. Brass alloys containing less than 14% of zinc will oxidise at the same rate as copper and the oxide film will contain both zinc and copper in the same proportions as in the metal. Alloys containing more than 20% of zinc oxidise much more slowly, and the oxide film is made up almost entirely of zinc oxide. It may be assumed that the zinc arriving in excess at the outer surface reduces the copper oxides to metal and preserves a uniform oxide film.[11] A similar action probably accounts for the slowing down of copper oxidation by the incorporation of aluminium, or of iron by the addition of chromium. Although the metal ions usually migrate outwards faster than oxygen or OH^- ions can diffuse inwards, active inward diffusion is known, and silver alloys can form small nodules of oxide at grain boundaries inside the metal when heated in oxygen. A balance of relative rates of diffusion will probably decide where and how reaction with a film-forming element will occur.

As with cathodic inhibition, any reactant in solution which gives a precipitate in the anodic region will check migration of the metallic ions and thus diminish the solution potential of the metal. Many hydroxides are sparingly soluble, and basic solution conditions can thus check reaction at anode and cathode alike. The anodic action is by precipitation of metallic hydroxide as soon as the metallic ions form. When a steel strip is partly immersed in a dilute solution of NaCl, corrosion proceeds more or less evenly over the immersed section, with a cathodic protection zone at the aerated water line. The addition of small quantities of Na_2CO_3 gradually reduces and localises the corrosion into small spots at very active areas—no steel is perfectly homogeneous—and continued addition of the alkali finally checks attack altogether. Just before this final inhibition, a very rapid attack may develop along the water line, with localised pitting on an area which had hitherto been unaffected.[12] This is due to the attraction of ferrous hydroxide membranes into the metal–water–air interface, removing the protective skin and forming a small anodic area. The upper surface of the detached hydroxide skin can form the cathode and the small resistance due to close proximity allows of rapid attack. It should be mentioned that although the lifting of anodic hydroxide film is generally considered to be the cause of localised corrosion, an impoverishment of inhibitor in the cranny between metal and solution has been suggested as an alternative.[13]

Although this edge effect is not confined to the action of anodic inhibitors, it is probably most dangerous when corrosion has been checked by these agents. The attachment of a ferrous hydroxide or oxide film is particularly easy to break, and as a result anodic protection of iron is only efficient when other compound-forming agents are present. A deep blue-coloured oxide film can be produced on steel by controlled oxidation in steam, and this is the most stable form of oxide available. Protection is quite inadequate for even mildly corrosive solutions, and only suffices for indoor atmospheric conditions. There is, however, a wide range of salts which confer a degree of anodic immunity on iron as well as other metals. The most important are the chromates, which in quite dilute solution (1–2 gm./litre) form a hard dark-coloured scale over any steel surface and check the corrosive effects of all aerated neutral solutions. Refrigerator brines, made up from calcium or sodium chlorides, are usually treated in this way, and can then be handled quite safely in cast iron or steel. Chloride solutions are normally the most corrosive agents met with in industry, probably owing to the ease with which a chloride ion can penetrate an anodic inhibitor skin, forming soluble salts, and lifting the protective film. Other acid ions are more easily checked, especially if they tend to repair a film by secondary action. The protection of aluminium by its own oxide in the presence of strong nitric acid is a typical example. Again, aluminium metal is attacked by alkalies in solution, as the inhibiting oxide film is broken up, but if the alkaline solution contains a trace of silicate, it is necessary to go to high temperatures and concentrations before the corrosion becomes serious. Undoubtedly the silicate is replacing an oxide by a salt film which is much less soluble. It is possible that the action of an inhibiting agent is to promote formation of an even and continuous oxide film. Wormwell and Mercer[14] consider that sodium benzoate acts in this way on mild steel. At any rate a benzoate skin is not formed, nor does a deficiency give that intense local pitting which follows a shortage of chromate ions.

The phenomenon of "passivity", noted long ago in the case of iron immersed in concentrated nitric acid, was explained by Faraday (1844) as due to a resistant skin of oxide, and there appears no reason to change this conclusion today. It may be that the film is one of adsorbed oxygen rather than oxide, but there is no clear distinction between such "passivation" and anodic inhibition by such salts as potassium chromate. An "electron configuration" theory has been propounded which proposes that a stable surface structure will not easily lose electrons by entering into solution, while an unstable surface may lose electrons to a receiver such as oxygen, fixing the oxygen as a film in the process. Obviously the physical nature of a surface will determine the character of any primary film that is formed, and this electronic linking is merely a restatement of

Faraday's original explanation in slightly different terms. Certainly the state of the metal surface is very important, and the thickness of the films involved can be small. Wormwell and Ison[15] show that the rate of corrosion of a steel specimen in dilute NaCl solution is largely determined by surface preparation. Cleaning by emery cloth gives a more resistant surface than grit-blasting, as shown in Fig. I-3, while an occasional specimen from the former treatment shows quite abnormal passivity. Similarly, the author has noted that stainless-steel valves, handling hot concentrated nitric acid, have an effective working life which is almost proportional to the time taken for grinding working surfaces to a good machine finish. Ordinary lap grinding with a single emery powder gives a valve which is tight for about 14 days, while a carefully finished surface, prepared by using three grades of grinding paste, will last from three to six months.

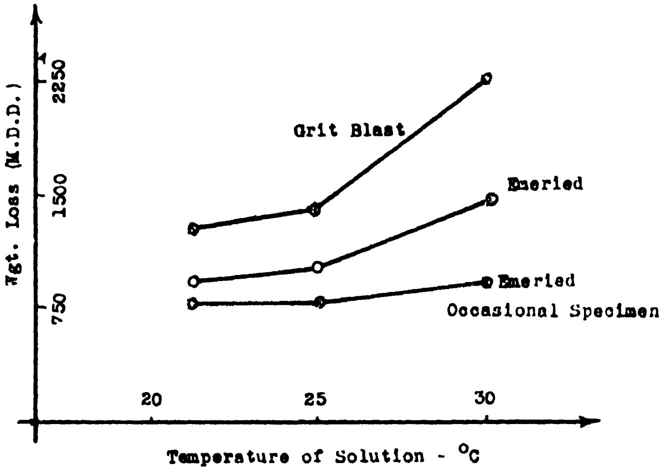


FIG. I-3.

(After Wormwell & Ison, *Chem. & Ind.* 1951, p. 293.)

CATHODIC PROTECTION ✓

When corrosion cannot be checked easily by inhibition at one or other of the electrodes, it may become politic to sacrifice some cheap metal, chosen to be strongly electronegative to the plant to be protected. Alternatively, an external electromotive force may be impressed on the system, using a sacrificial anode or liberating oxygen, with the plant as cathode. The first process is now being very widely used in the protection of buried pipe-lines. Long lengths of pipe, which should ideally be at the same potential throughout, are connected at intervals to blocks of zinc or magnesium buried in the same soil. Under ideal conditions, all corrosion could be centred in one block of the sacrificial metal, but in practice it is necessary to attach blocks at fairly frequent intervals. A certain minimum current density is required at the pipe if local attack is not to be set up, and clearly the influence of the anodic block will be most marked at the pipe regions nearest to it. Again the anodes should be of metal which is as pure as possible, or local corrosion cells will be set up and the blocks wasted away without giving pipe protection. Zinc, perhaps the most commonly used metal, will build up an insulating coating in some carbonate-rich soils, and it is better to bury the blocks in a special environment of clay and gypsum. Magnesium does not tend to form protective coatings, but is more costly than zinc. As a general rule, anodic blocks should be buried within 10 feet of the pipe, and spaced at distances from 100 to 500 yards according to the nature of the soil. Protection of this kind is especially valuable in soil of high conductivity, or in flooded conditions. When the soil resistivity is high—above 2500 ohms/c.c.—it is better to use external e.m.f. application.

A constant current output transformer-rectifier sets up a steady potential difference between the plant to be protected and a buried anode, which may consist of scrap iron, graphite, or metallurgical coke. Iron is most generally used, as being easiest to connect electrically, and a potential of about 1 volt between plant and anode is quite adequate for protection. Special methods[16] have been devised for the protection of current-carrying rails and similar electrical plant, but are not within the scope of this book. The placing of suitable anodes within a chemical plant of complex form presents many difficulties, though storage water tanks have been protected successfully. Intensive chemical attack can hardly be checked without very large expenditure on current, but the process appears to be economically sound when applied to buried iron pipes.

DIRECT CHEMICAL ATTACK

It is true that most examples of corrosion are due to electrolytic action, at any rate in the case of metals, but reaction can occur in the apparent absence of ionising solutions. When a clean iron surface is heated in dry air or oxygen, it does not change in appearance until temperatures above 200° C. are reached. Then a film of oxide appears on the surface, changing in colour from yellow to blue and finally to grey, before the whole surface becomes visibly red. Other metals behave in the same way, although the rate at which the oxide film forms will vary widely. The thickness of the oxide generally increases with time in accordance with three different relations:

(1) The gain in weight may be linear, or

$$W\ (\text{weight}) = K.T\ (\text{time}) + C$$

where K and C are characteristic constants. Reaction rates are probably governed by the speed of diffusion of active oxygen molecules to the metal surface, with the existing oxide film offering little resistance. It is a reasonable assumption that the first stage in oxidation is the adsorption or chemisorption of oxygen at the active metal. Linear rate of reaction suggests either an incomplete oxide film *or* rapid diffusion of the reactants in the formed film.

(2) The gain in weight may vary inversely with the amount of oxide already formed, or

$$W = K\sqrt{T} + C$$

The rate is presumably determined by speed of diffiusion of either oxygen or metal through a continuous oxide film, and is a parabolic function of the total amount of reaction.

(3) The rate of gain in weight falls off inversely as some positive power of the amount of oxide formed, or

$$W = K \log T + C$$

This suggests that the initial oxide film forms only slowly, but as the gaps fill, the completed membrane is impermeable to all possible reactants.

Now a film of oxide growing on a metal may be represented as an electrolytic cell, with the metal as anode, the outer surface of the skin as cathode, and the film itself as an electrolyte. Metallic ions and electrons pass outwards from the metal, while anions from the cathodic side, either OH^- or O^{--}, pass inwards, as suggested in Fig. I–4. The film acts as both internal and external resistance of the cell, while e.m.f. is provided by the oxidation reaction. As this latter is constant, the amount of current passing, and hence the extent of the reaction in a given time, will be proportional to the film resistance. But it will also be affected by the time taken for oxygen to arrive and to assume a reactant form on the cathodic side, and in certain cases this latter effect may determine almost completely the rate of oxide formation. If these views are correct, there is only a difference in degree between the three forms of growth set out above, and the one type may pass into the others by variation of temperature or some alternative experimental condition. This is certainly the case for aluminium, which oxidises very slowly

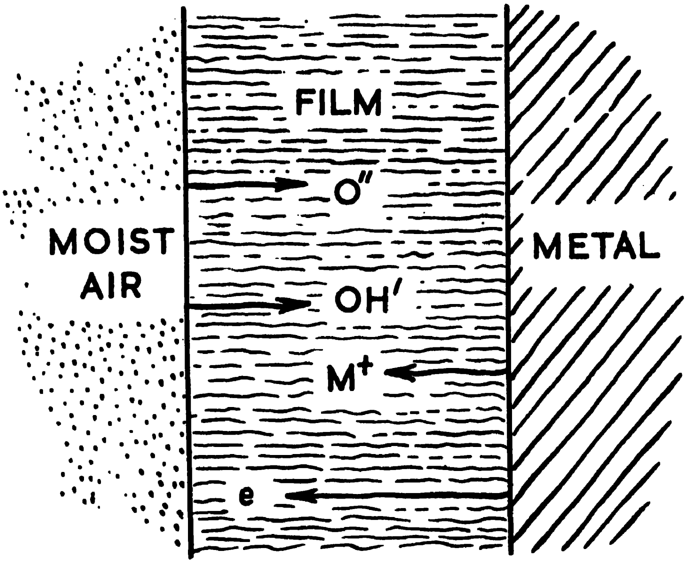


Fig. 1–4.

indeed in air at ordinary temperatures. When the temperature is raised to 400° C., the rate of oxidation is much faster and appears to follow a parabolic law of growth. Finally, at about 500°, the rate becomes linear.[17] It is known that the initial oxidation of a *clean* aluminium surface is very fast indeed, and a protective film forms in a few seconds. In this period, even at ordinary temperatures, the rate of growth can only be determined by the speed of arrival of oxygen at the metal surface, and will be linear. Copper at a temperature of 200° C. oxidises at first in accordance with a parabolic law, though the very first stages, as with aluminium, must be linear. As the copper oxide film grows, there is a gradual change to logarithmic growth.[18] Zinc in similar conditions reverts almost immediately to a logarithmic rate of oxidation, while magnesium continues to react at a steady linear rate. It is probable that all metals follow the reaction pattern shown in Fig. I–5, with the initial rates determined by oxygen arrival and activation, the intermediate parabolic form governed by diffusion through a conducting film, and the final logarithmic decrement caused by a compacting or completing of an almost impermeable membrane. The phenomena resemble the filtration of a compressible slurry at steadily increasing pressure, with initial rates determined by filter-cloth resistance, steady diminution due to cake resistance, and a further decrease due to compacting which may stop filtration altogether. For some metals, as with sludges, the resistance of the cake will not alter by compacting, and hyperbolic rates of oxidation continue indefinitely, while with others the film resistance will be so slight that oxide formation will continue to be governed by the rate of arrival of oxygen at the surface.[19] It is possible that the resistance of the film to further oxide formation is coupled with electrical properties, and that the most protective film is that which shows the highest electrical resistance.

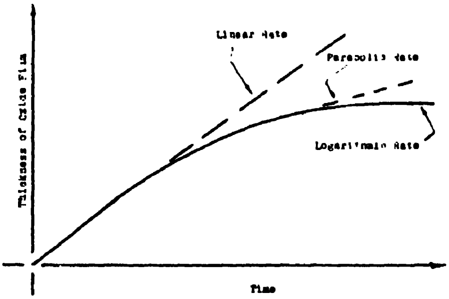


FIG. I–5.

The above paragraphs have perhaps presented an over-simplified picture of direct oxygen attack on metals. Many films are complex, containing for multivalent metals several forms of oxide. Copper forms only a cuprous oxide until the film grows thick enough to check the rush of copper to the surface, when a cupric oxide appears. Iron films can contain FeO, Fe_3O_4, and Fe_2O_3 at high temperatures, but at lower levels the mobility of the metal ions is so checked that only Fe_2O_3 appears, even immediately adjacent to the metal surface. The varying rates of diffusion shown by different metallic ions in the same oxide lattice have already been referred to, and it is possible that the protective effect given to many metals by the addition of aluminium or chromium is due to the impermeability of oxide films built up from these metals. A *pure* alumina film, in particular, has been shown to have very high resistance to ionic penetration.[20]

The attack of other gases on metals, either in the presence of air or alone, probably follows the same general pattern as with oxygen. Combination of two gases can be more potent than either alone, as shown by the effect of small quantities of sulphur-bearing gases on oxidation rates. The presence of 5% SO_2 in air trebles the rate of attack on mild steel at 900° C., while traces of H_2S will catalyse a steady air attack on copper at ordinary temperatures. It may be that a sulphur complex is formed and later oxidised to a porous oxide film, or that a variation in crystal structure is caused by the presence of these gases. At high temperatures a sulphide–oxide eutectic will melt at a much lower level than a pure oxide, and can float off a lighter oxide film from the metal. The effect of moisture on all reactions is, of course, well known, but steam alone is a very corrosive agent at high temperatures, and even more troublesome when associated with sulphur-bearing gases at temperatures low enough to reach a sulphuric acid dew-point. This, however, is liquid-phase corrosion of the normal type. Thompson and Ubbelohde[25] have recently discussed the mechanism of direct non-ionic attack by gases on metals.

STRESS CORROSION ✓

This phenomenon is the combined effect of mechanical stress and corrosive conditions, and almost invariably takes the form of a very localised attack resembling cracking. The corrosion lines appear to follow crystal boundaries, and it is considered that the initial attack is on the slightly more reactive atoms at these points, producing a microscopic crack or enlarging one which has already existed. Then, just as in the failure of any cracked section when put under stress, a very high local stress concentration is produced at the bottom of the crack. This increases the reactivity of the molecules, or pulls the crystal faces further apart, and corrosion proceeds to deepen the fissure still further. Where a passivating film, either at the anode or cathode of the corrosion cell, has been formed it may be less elastic than the underlying metal and will crack in places where the metal crystals are tending to slide apart. Then the underlying area will be anodic to the rest of the surface and preferentially corroded. However, it will normally be expected that such an attack will be less confined to crystal boundaries than one by the former mechanism, which is the explanation generally preferred. In support of this, it has been found that many anodic inhibitors also check stress corrosion, presumably by healing over the initial surface cracks wherever they exist or are formed.

When a piece of metal has been "cold-worked" or deformed in some way at temperatures which are too low to allow free movement of the atoms in the metal, it is almost certain that internal stresses exist. For example, in a cold-drawn wire the outer skin is in tension, while the centre is in compression, owing to the expansion of the wire as it leaves the dies. A similar state of affairs exists in a vessel under internal pressure, and in fact a fracture usually starts in the outer layers. Stress corrosion, then, may be looked for whenever a section of plant has been assembled by cold-working, as in riveting, or where a definite stress has been applied, as in screwing up a nut to tightness at a joint.

In the most dangerous "cracking" form of stress corrosion, the base of a crack has become anodic to the rest of the metal, but the very shape of the pit suggests that it may readily become choked with corrosion products unless these are fairly soluble. In accordance with this, iron in neutral solution does not show any increase in corrosion when stressed. When conditions are acid, however, and the iron salt is soluble, corrosion rates are greatly increased, with mechanical failure occurring when the stress is maintained at loads well below the normal breaking point of the metal. Perhaps the most disastrous form which this attack has taken with iron has been in the "caustic embrittlement" of riveted boilers, which will be dealt with in a later section. Here the iron is taken into solution in the caustic soda which is attracted to the crannies of the boiler shell.

The effect of alternating stresses, combined with corrosive conditions, leads to failure in exactly the same way as a static stress, though generally referred to as "corrosion fatigue". Metal parts for carrying varying loads are generally required to possess a "corrosion fatigue limit" well above the load for which they are designed. This limit is the maximum alternating stress which will not cause failure after a fixed number of stress cycles—usually a million. Under corrosive conditions the stress may be well below the ultimate tensile strength. A mild steel, having a normal strength of 40,000 lb./sq. in., will show limits of 20,000 lb. in fresh water and 7000 lb. in a dilute NaCl solution. Sharp changes in section, or grinding scratches, can still further lower the fatigue limit, and it would certainly appear that the mechanism of failure is identical with normal stress corrosion. None the less, it has been shown[21] that failure in fatigue is often across crystal boundaries, as distinct from the ordinary intercrystalline cracking which might be expected.

Whatever the action, it is certainly through normal corrosive attack, and can be checked by addition of inhibitors such as chromates, or even by painting. The effects are most marked in metals with a very high ultimate tensile strength under normal conditions. Probably these have a somewhat reactive work-hardened form, which would appear at the bottom of fissures in which stresses are concentrated and check further failure. Now if corrosion removes this reactive metal as it forms, the causes for failure are all present.

EROSION-CORROSION

The effects of rapid movement in allowing (*a*) free diffusion of reactive ions to the surface and (*b*) rapid removal of local metal ion concentrations must normally increase corrosion. Although oxygen may diffuse to build up an oxide film, this can be rapidly removed by any form of mechanical abrasion. During the 1914–18 war, it was found that condenser repairs immobilised more warships than did any form of enemy action. This was due to localised attack on the brass condenser tubes then in use, initiated by the impingement of entrained air bubbles. Copper or zinc oxide films were worn away, and a preferential attack on the zinc followed. A combination of improved design of water inlets and the incorporation of aluminium into the alloy to give a more resistant oxide skin all but eliminated "condenseritis" of warships during the war of 1939–45.

The rapid motion of metal parts, as in pumping, can not only lead to erosion by the liquid streams, but to the phenomenon of 'cavitation,' or the formation and collapse of gas bubbles by pressure variation. Again, the bearings of a pump handling acid are subject to rubbing friction in the presence of a corroding fluid. In these circumstances it is almost impossible to avoid localised corrosion, and fortunately these areas are small, with the possibility of manufacture from special materials. Differences of potential can also be set up by liquid movement, probably by a form of metal erosion, and these can bring about unexpected corrosion effects. Copper, in particular, is subject to this form of attack, and failures in an evaporator system have been shown[22] as due to "moto-electric effects".

The above pages have given a general outline of corrosion theory. The resistance of specific materials to attack will be dealt with in the chapters following. For a very comprehensive treatment of metallic corrosion the reader might consult the well-known treatise[23] by U. R. Evans, already referred to on several occasions, while the same author's shorter work[24] presents a reasonable picture without the masses of data set out in the comprehensive treatise.

REFERENCES

1. Evans, U. R., *Chem. and Ind.*, 1951, p. 706.
2. Hickling, A., and Salt, F. W., *Trans. Farad. Soc.*, 1942, **38**, 474.
3. After Knobel *et al.*, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 55.
4. Powell, S. T., *et al.*, *Ind. Eng. Chem.*, 1945, **37**, 842.
5. Raistrick, B., *Chem. and Ind.*, 1952, p. 408.
6. Chappell, E. L., Roetheli, B. E., and McCarthy, B. Y., *Ind. Eng. Chem.*, 1928, **20**, 582.
7. Mears, R. B., and Brown, R. H., *Ind. Eng. Chem.*, 1941, **33**, 1009.
8. Evans, U. R., "Metallic Corrosion, Passivity and Protection", 2nd Edn., E. Arnold and Co., 1946, p. 592.
9. Vernon, W. H., *et al.*, *J. Chem. Soc.*, 1939, p. 621.
10. Evans, U. R., and Tomlinson, R., *J. Appl. Chem.*, 1952, **2**, 105.
11. Dunn, J. S., *J. Inst. Metals*, 1931, **46**, 25.
12. Evans, U. R., "Metallic Corrosion, etc.", *loc. cit.*, p. 550.
13. Thornhill, R. S., *J. Iron Steel Inst.*, 1942, **146**, 94.
14. Wormwell, F., and Mercer, A. D., *J. Appl. Chem.*, 1952, **2**, 150.
15. Wormwell, F., and Ison, H. C., *Chem. and Ind.*, 1951, p. 293.
16. Symposium on Corrosion of Buried Metals, Iron and Steel Inst. (Dec. 1951)
17. Gulbransen, E. A., and Wysong, W. S., *J. Phys. Coll. Chem.*, 1947, **51**, 1087.
18. Dighton, A. L., and Miley, H. A., *Trans. Electrochem. Soc.*, 1942, **81**, 321.
19. See, e.g., Evans, U. R., "Metallic Corrosion, etc.", *loc. cit.*, p. 134.
20. Price, L. E., and Thomas, G. J., *J. Inst. Metals*, 1938, **63**, 21.
21. Inglis, N. P., *Trans. N.E. Coast Inst. Eng.*, 1939, **55**, D.33.
22. Inglesant, H., and Storrow, J. A., *J.S.C.I.*, 1945, **64**, 233.
23. "Metallic Corrosion, etc." See Ref. 8, above.
24. "An Introduction to Metallic Corrosion", E. Arnold and Co., 1948.
25. Thompson, F. W., and Ubbelohde, A. R., *J. Appl. Chem.*, 1953, **3**, 27.

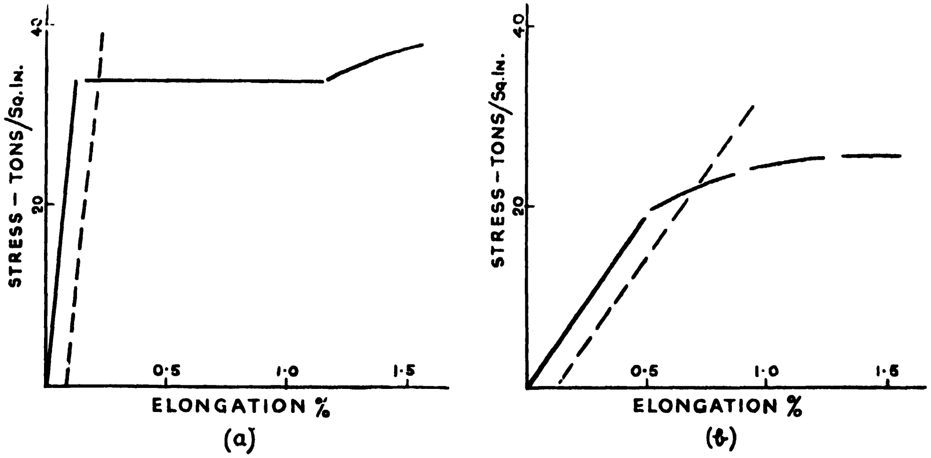
CHAPTER II

TESTING OF CONSTRUCTIONAL MATERIALS

ULTIMATE TENSILE STRENGTH

THE first essential of any material used in the manufacture of chemical plant is that it shall not be rapidly attacked by the chemical. The second essential is that it shall be mechanically reliable, or as reliable as is compatible with the corrosion resistance required. All solid materials deform elastically when put under a small stress, and the ratio of deformation (strain) to stress is practically constant as the stress increases, until the elastic limit of the material is reached. Up to this point the material is almost perfectly elastic, the strain disappearing when the stress is removed. When the stress is increased beyond this elastic limit, plastic deformation of a more permanent character occurs. Deformation remains after the stress is removed, will continue to increase if the stress is kept constant, and will ultimately cause mechanical failure. The "elastic limit" ("limit of proportionality stress") is defined in specifications[1] as the stress per unit area of material at which the strain, or elongation per unit of original gauge length, ceases to be proportional to the corresponding stress.

It is probably true that no perfectly elastic material exists, and that any stress produces some permanent deformation, even though this may be immeasurably small. Typical curves for tensile stress *v.* strain, as shown in Fig. II–1 for samples of (*a*) mild steel and (*b*) aluminium, do show clear points of departure from an apparently linear relation, especially with the former. More exact measurements have shown, however, that true proportionality is never quite attained, and for this reason it is now general to specify a "proof stress" rather than an elastic limit. The proof stress is defined as the stress at which the stress–strain relationship departs from the straight line of exact proportion (Hooke's Law) by some fixed amount, normally set at an abnormal strain of 0·1% of the test-gauge length. As shown by the dotted lines in Fig. II–1, this proof stress will be about 34 tons for the steel and 24 tons for the aluminium. The rapid extension of steel at its elastic limit has suggested a further term—"yield stress", or stress at which elongation occurs without increase in load. This is subject to the same criticism as "elastic limit", and is usually confined to tests on steel.



(a) (b)

FIG. II–1.

When a metal or metallic alloy is stressed beyond elastic limits, as to some point A_1 in Fig. II–2, and the stress is removed, the specimen may return to normal unstressed conditions in a way represented by the line A_1X_1. Then re-application of the stress gives elongation back along X_1A_1 to a higher elastic limit and a correspondingly higher proof stress. The change is commonly accompanied by a hardening of the surface of the metal, and is therefore known as "work-hardening" or "strain-hardening". Any form of mechanical work done on the surface layers of many metallic materials produces this increase in hardness and strength. Copper is the best known example of this group of metals. In a soft annealed form, given by heating to 500° C. and cooling, copper has a very small proof stress and no real elastic limit. Simple hammering, as in coppersmith's work, produces a tough, hard

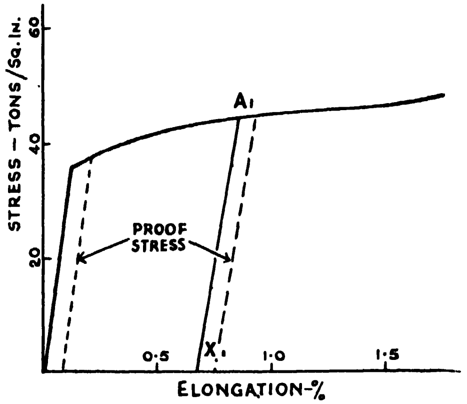


FIG. II–2.

material with a proof stress as high as 20 tons/sq. in. Tensile-tests on the annealed metal are somewhat uncertain as the metal is steadily hardening under the testing stress.

It will be appreciated that a stress–strain curve, as set out in the figures above, does not include any time factor, and theoretically can only be correct when the material is perfectly elastic. Tests on such an easily work-hardened material as copper illustrate this point. When the load on the test specimen is increased slowly, much higher figures are obtained for the proof stress than when a rapid test is made. All measurements of tensile strength must therefore be carried out under standard conditions, with the proof stress increasing at a steady rate. Hand-operated machines have now been almost completely replaced by motor-driven units for this reason. A typical tensile-strength testing machine is shown in Fig. II–3. The test-piece is held between a fixed base and a movable head which is forced upwards by a hydraulic ram. Liquid (normally a light oil) is pumped simultaneously to the ram and an

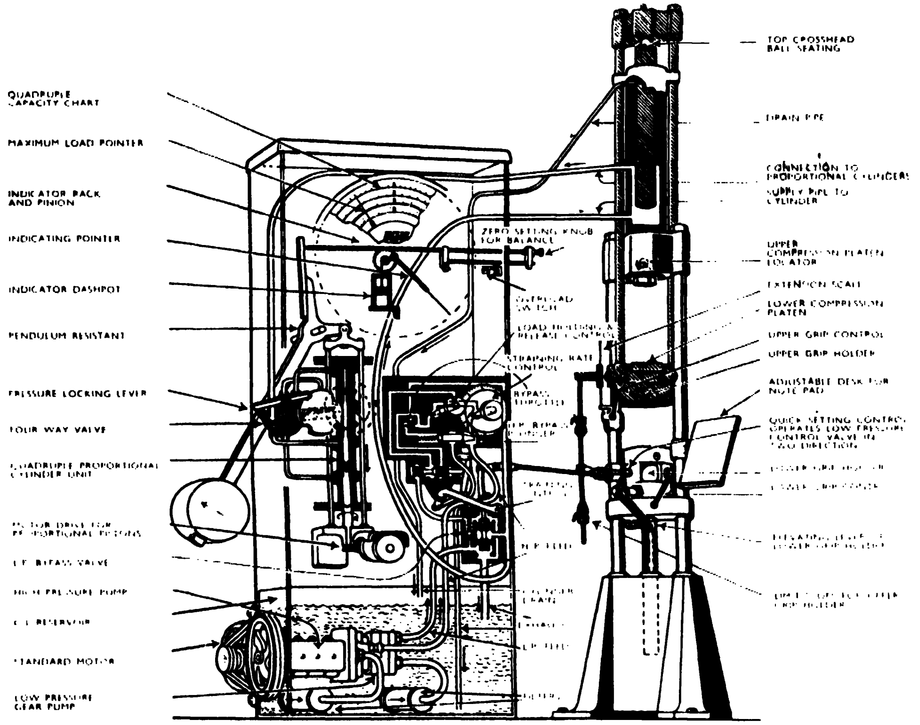

QUADRUPLE CAPACITY CHART
MAXIMUM LOAD POINTER
INDICATOR RACK AND PINION
INDICATING POINTER
INDICATOR DASHPOT
PENDULUM RESISTANT
PRESSURE LOCKING LEVER
FOUR WAY VALVE
QUADRUPLE PROPORTIONAL CYLINDER UNIT
MOTOR DRIVE FOR PROPORTIONAL PISTONS
L.P. BYPASS VALVE
HIGH PRESSURE PUMP
OIL RESERVOIR
STANDARD MOTOR
LOW PRESSURE GEAR PUMP
ZERO SETTING KNOB FOR BALANCE
TOP CROSSHEAD BALL SEATING
DRAIN PIPE
CONNECTION TO PROPORTIONAL CYLINDERS
SUPPLY PIPE TO CYLINDER
UPPER COMPRESSION PLATEN LOCATOR
EXTENSION SCALE
LOWER COMPRESSION PLATEN
UPPER GRIP CONTROL
UPPER GRIP HOLDER
ADJUSTABLE DESK FOR NOTE PAD
QUICK SETTING CONTROL OPERATES LOW PRESSURE CONTROL VALVE IN TWO DIRECTIONS

FIG. II–3.—DETERMINATION OF ULTIMATE TENSILE AND CRUSHING STRENGTHS. (*Courtesy Messrs. Avery, Ltd.*)

"Diamond Pyramid" or "Vickers" hardness measurements. In this test the load is applied to a diamond point ground to square pyramid section with an included angle of 136°. As with the earlier tests, it is necessary to standardise load and time of application, while the area of the impression is again determined microscopically.[5] To overcome the resulting slowness, direct-reading machines have been devised for measuring the depth of an impression and recording this on a dial. These are known as Rockwell direct hardness testers, and use three different penetrators, giving three scales of hardness.[6] Comparison between Moh's scale, Brinell, Diamond Pyramid and Rockwell hardness numbers is made in Table II–1 below. A "cloudburst" test has been sometimes used, in which a rain of steel shot, over a comparatively large area, etches out any soft portions of surface which might not be detected by impression tests.

TABLE II–1

Moh's Scale	Brinell No.	Diamond Pyramid No. (Vickers)	Rockwell Hardness		
			A	B	C
Talc	10				
	20	20			
sum	50	50			
Spar	95	100	43	54	
par	195	200	59	94	
te	295	300	66		30
dspar	535	600	77		54
Quartz		800	82		62
Topaz		1100			
Sapphire		2100			
Diamond					

See also B.S. 860 (1939) which sets out tables of comparison between the last three scales.

As mentioned above, the tensile strength of a number of metals, particularly in the ferrous alloy group, can be approximately calculated from the hardness. A general relation between Brinell number (*Br*) and ultimate tensile strength (*S*) in tons/sq. in. can be used in the form

$$(S) = k \times (Br)$$

where k, the experimental constant, varies from 0·22 for steel to 0·35 for copper alloys. The relationship is purely empirical and of doubtful value.

FATIGUE

The failure of a solid can occur through repeated application of a cycle of stressing load, even though the magnitude of each individual load may be well within the elastic limit of the material. Most severe conditions are given by a variation from tensile to compressive stress, but a good constructional metal will withstand vibrating loads of this type indefinitely, providing that each individual stress does not exceed a certain critical value known as the "fatigue limit". A very small number of stress cycles will cause failure if the applied stress is near the ultimate tensile strength of the metal. As the stress decreases, the number of cycles the specimen will withstand increases, as shown in Fig. II–6, until at the fatigue limit the curve becomes horizontal. Curve (*a*) is for a mild steel, while (*b*) is for a constructional aluminium alloy. As will be seen, the form of the fatigue failure curve varies notably, and for some metals no true limit can be established. For this reason it is quite general to specify a "fatigue strength" or "endurance limit" of so many tons/sq. in. after a given number, normally 10^6, of cycles. The endurance limit can be greater or less than the elastic limit, and is commonly from $\frac{1}{4}$ to $\frac{1}{2}$ of the ultimate tensile strength.

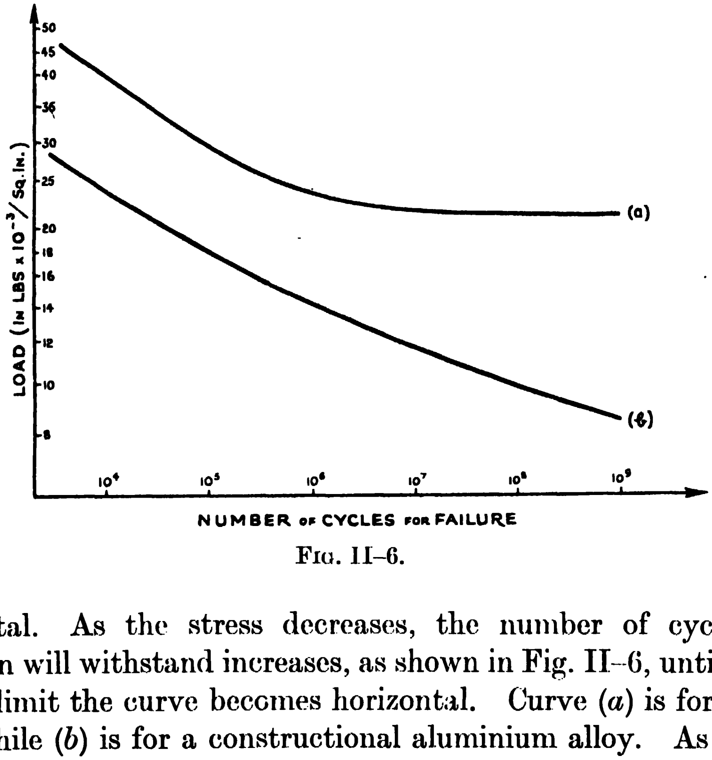


FIG. II–6.

The usual machine for testing fatigue is the Wohler Rotating Cantilever. The specimen, turned to a short cylinder, supports a ball bearing on which a weight is hung. Then rotation puts alternate tensile and compressive stress on each part of the outer fibres of the cylinder. These tests are very susceptible to slight changes in external conditions, particularly when corrosion may be involved. When fatigue tests are carried out *in vacuo*, many, though not all, metals show a considerably higher limit.[7] A mild-steel specimen can show endurance limits of 35,000–40,000 lb./sq. in. (at 10^6 cycles) when tested in air, but the same steel in a natural water gives only about 20,000 lb./sq. in.[8] More corrosive media will have still greater effects, as mentioned in the previous chapter.

In the design of chemical plant it is seldom necessary to consider mechanical properties outside the range of those detailed above. The typical chemical plant is made up from a series of containers for the reactants, combined with devices for moving them from one vessel to another. Design, for corrosion-resistance reasons, will generally be as simple as possible, and the problems of weight–strength ratio or of complicated loading are seldom, if ever, encountered. Plant is not mass-produced, so that the ease with which pressing or spinning may be carried out is unimportant, and a generous safety factor is allowable. A useful summary of mechanical tests on metals is given in B.S. Handbook 13 (1951).

CORROSION RESISTANCE

Tests for corrosion, on the other hand, cannot be too careful or extensive. It is a fundamental weakness of all laboratory tests on small samples of material that plant conditions cannot be fully reproduced. In the first place there is no way of obtaining a representative sample of the whole structure of a plant. If two steel plates are welded together, or riveted at a tank corner, then samples of the plate will give no guide as to the behaviour of the joint. In very critical conditions, such as the welds for a boiler shell, it is customary to extend the welds on to test projections, which are then cut off for testing, but even this does not really "sample" the whole welded boiler. Again, corrosion is normally measured as a change in weight of the specimen being tested. This gives no indication of the nature of the attack. If the surface of a steel plate is uniformly dissolved at a rate of 100 milligrams per square decimetre per day, this would mean that the plate would waste away at a rate of 0·02 in. of thickness per year. Then a container built of $\frac{3}{8}$ in. plate would still have an effective thickness of over $\frac{1}{4}$ in. at the end of five years.

But in actual practice such a corrosion rate would mean that the plate would be holed locally long before the five years were up. Almost all corrosive attack on ferrous alloys is localised, and the same is true for many other metals. No unit of chemical plant dissolves away, but it can and does develop leaks which make it unfit for service. At the same time, attempts to measure "pitting", which indicates this penetrative form of chemical attack, are essentially only true for the test specimen, especially where the parent plant may be under some form of mechanical stress. Aeration and trace contaminants peculiar to plant operation can hardly be reproduced in a laboratory, and these have been shown all too often to control corrosion. As a result it has been generally considered that the only reliable corrosion test is the one which gives an emphatic negative to the question of use. Yet stainless steel is steadily attacked by cold dilute sulphuric acid when tested in a laboratory, but on a works can last for many years in contact with the same reagent. It is not possible, however, to build a costly plant in order to demonstrate the suitability of some material of construction, and despite these disturbing facts some form of corrosion test must be applied.

Specimens of the material to be tested are exposed to the appropriate reagent, and as a rule the results obtained are expressed in terms of weight loss from the cleaned and dried specimen. These are given in the tests set out below as "milligrams per square decimetre of surface per day of 24 hours"—abbreviated to "mdd". An alternative form, which many workers prefer, is a loss in thickness, or a penetration of so many inches per year—abbreviated to "ipy". These two ways of expressing loss can be correlated by the general expression

$$\text{mdd} = \text{ipy} \times \varrho / 0{\cdot}00144$$

where ϱ is the density of the metal being tested in grams/cubic centimetre. If ϱ is measured in pounds per cubic inch, then the general expression becomes

$$\text{mdd} = \text{ipy} \times \varrho / 0{\cdot}000052$$

For most ferrous alloys, a near enough approximation is given, for all practical purposes, by the form 100 mdd = 0·02 ipy.*

Again it must be stressed that such figures give no indication of the depth of local pits. These may be measured by a micrometer needle, contact of the needle point with the metal at the base of the pit being registered electrically. It is doubtful if such a test will be of great practical use, as any material on which obvious pitting had occurred would be rejected without further ado. In any case, the needle method would not be suited for intergranular cracks, or for microscopic pinholes.

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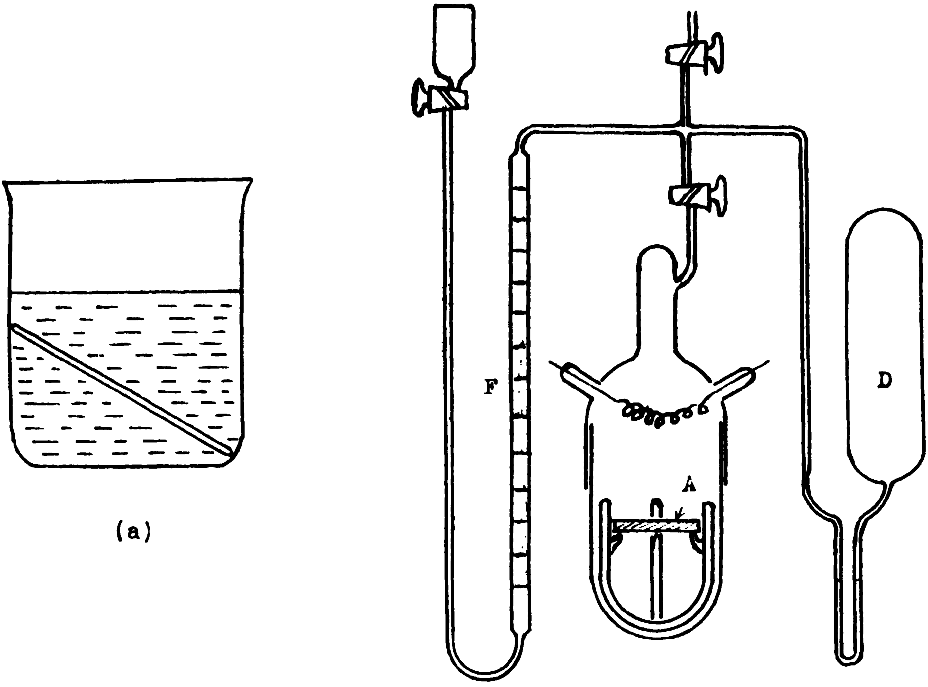
* For light corrosion, results are sometimes quoted as "mils/year" or thousandths of an inch penetration per year.

The simplest way to carry out corrosion tests is to immerse the specimen in the corrosive medium. Unless the plant is to be operated under abnormal conditions, air should be present, and free diffusion through liquid layers to the test specimen must be ensured. A criticism that is often launched at these measurements is that "edge" effects may predominate. Where a metal is normally protected by a continuous film of some kind, this will be broken by cutting a small piece for trial, and attack, starting at the edges, will lift the protective coating. This may not be a disadvantage, as indicating the possibility of such action taking place in the plant, but as a rule it is considered preferable to protect the edges by coating



(a)

(b)

Fig. II-7.—Corrosion Testing.

(After Vernon, *Trans. Inst. Chem. Eng.*, 1939) with waxed paper or stoving varnish. The test-piece should then be supported so that it does not lie flat at the bottom of the container. There is usually no reason for any more elaborate set-up than that shown in Fig. II–7*a*, though the beaker should be of hard glass with a low solubility for most acids, or of polythene for HF solutions. For exact theoretical work devices such as that shown in Fig. II–7*b* may be built up. The bulb D is adjusted to constant pressure through the oxygen burette F, while traces of hydrogen can be burned off by a platinum wire loop. The test specimen A is supported on glass points, and has been prepared by machining to definite dimensions.

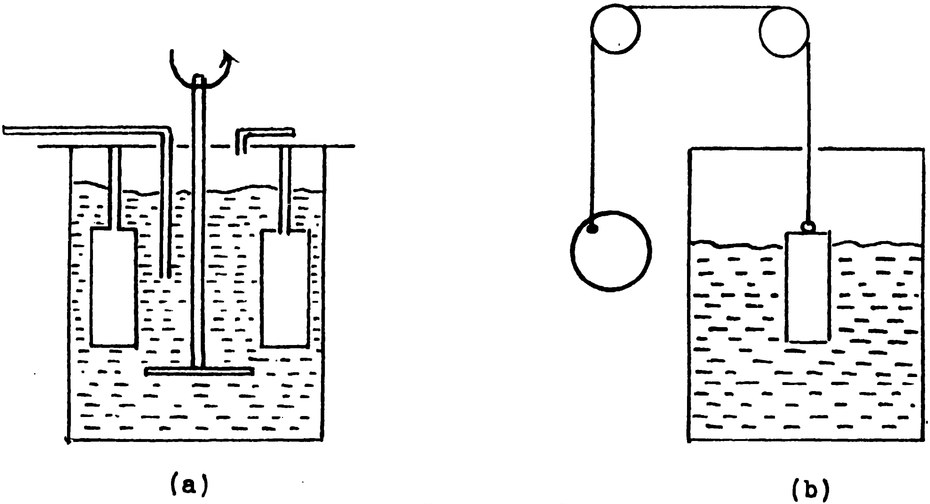

(a) (b)

FIG. II–8.—CORROSION TESTING.

When it is desired to test the effect of movement on corrosion rates, an apparatus such as that shown in Fig. II–8*a* is used. A strip of the test material cemented to a rotating glass rod, or some other inert support, and moving with a peripheral velocity of about 15 feet per second, moves the corroding liquid round the stationary baffle strips, which can either be of glass or of the same material as the stirrer being tested.[22] A stream of air, or some other test gas, controls the degree of aeration, etc., in which the corrosion proceeds. Again, if it is anticipated that the plant will be frequently emptied, then the test specimen can be only partly immersed—a method for detecting "water-line" corrosion, or oscillated up and down, sometimes with a stream of drying air (Fig. II–8*b*) to give true wet and dry conditions.

In all tests it is vital that the temperature should be carefully controlled, and adjusted by thermostat to the levels expected in the actual plant. The actual skin temperature of a heating surface is often found to be well above the boiling-point of the surrounding solution, and this must be borne in mind when setting test temperatures. Mild steel is relatively unattacked by boiling 25% NaOH solution—a temperature of 240° F. A mild-steel evaporator used in this work was rapidly corroded, and the effect was traced to steam temperatures in excess of 300° F. When steam pressures were kept below 60 lb./sq. in. (293° F.) steel construction gave adequate resistance.

Possible changes in the rate of corrosion should be borne in mind and experiments should cover a long enough period to detect such alterations as are shown in Fig. II–9. In these tests, metals A, B, and C will all show the same loss in weight after a time *t*, but longer tests will show that only C is really suitable for plant work.

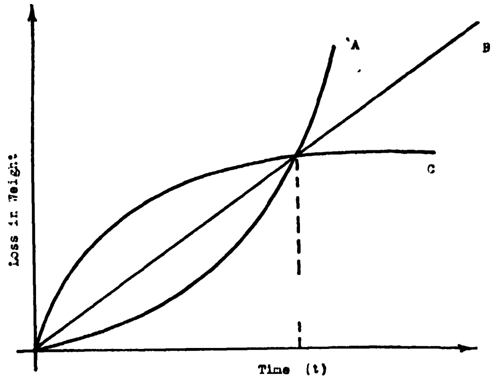


Fig. II–9.—Effect of Time.

In all this reasoning, loss in weight has been taken as the most important criterion of corrosion. Now the initial attack on the metal must cause a gain in weight by formation of a complex, even though this passes rapidly into solution. If an insoluble complex is formed, then it will be deposited on or near the metal surface, and must be cleared away before true weight loss can be estimated. A number of cleaning fluids and methods have been developed in the course of fundamental work.[9] For iron and steel, the specimen can be made the cathode in 5% NaOH or a similar solution of citric acid; a current of 0·2 amps/sq. in. for 3 minutes, using carbon anodes, suffices to strip off any deposits. Copper and brass can be cleaned directly with 5% sulphuric acid, and aluminium by 1–2% HCl solution. When the film is very difficult to remove, it will almost certainly be exercising a protective action, giving rates of attack similar to those shown in curve (C) of Fig. II–9. In such cases it may be better to measure the *gain* in weight of the test-piece, without any attempt at stripping.

These immersion tests are quite effective in the detection and estimation of surface attack, but cannot normally indicate "sub-surface" corrosion. Where pitting is clearly occurring, the micrometer needle mentioned above can be used, but a much more insidious form of damage—intergranular cracking—goes undetected. An almost negligible loss in weight may leave a fissure penetrating right through a stout metal wall. In a typical instance, the measured weight loss of aluminium in hot aqueous triethanolamine solution was less than 0·01 ipy, but when a coil of piping with a $\frac{1}{16}$-in. wall was used for the same solution, it was riddled with tiny holes in less than a week. This may have been a combination of normal intercrystalline attack with stress corrosion, as many examples of this latter process take the form of local cracking or opening of intercrystalline bonds under stress. Microscopic examination of the surfaces after test is always to be recommended, and many specifications call for a bending trial subsequent to corrosion by selected agents.[10]

Joints of any kind are a nucleus for attack, and full examination should include a jointed specimen in the corrosion testing. Welds are now the commonest form of joint, and a welded strip can easily be prepared. Riveted joints are unusual, but their behaviour can generally be simulated by tests on a strip of metal cold-bent to horseshoe form. Flanged joints will incorporate some form of gasket, and the material of this may combine with the chemicals in the plant to set up a local corrosion cell. When a stainless-steel pipe-line is being constructed for conveying very corrosive acids, it is always advisable to set up test units in which a strip of gasket material is pressed between steel strips as in the pipe-line proper.[11]

When very large and costly plant units are contemplated, attempts should be made to simulate plant conditions closely, even to the extent of building miniature plant. One of the valuable features of pilot scale work is that corrosion can be measured under actual operating conditions. Small evaporators and condensers can be built for testing, as shown in Fig. II–10, while experiments on the effect of high pressure can be carried out in sealed glass tubes, heated in iron sheaths. The corrosion of metal work can go on from the outside, as well as by specific chemical attack from within. In an extraction process using hot dilute hydrochloric acid, wood and rubber combined to give a corrosion-free plant, but the steel girders and roof work of the building had to be renewed after a year.

Adequate painting might have averted this damage, which could have been foreseen if metal specimens had been exposed to a suitable plant atmosphere. A "spray chamber" experiment, in which the test-pieces are hung in a spray-filled box, is the most usual control for atmospheric corrosion. Normal industrial atmospheres can be simulated with a spray made up from weakly acid sodium chloride solution. Swinden and Stevenson[12] suggest that N/100 acid in N/100 chloride makes a spray which, in air, corrodes to the same extent over 20 days as "field" exposure for a year. A more complicated spray suggested by Vernon[13] contains traces of sulphuric and sulphurous acids, with CO_2 to saturation. This is held to give a closer approximation to inland industrial practice, but different areas may have widely different atmospheric conditions. In

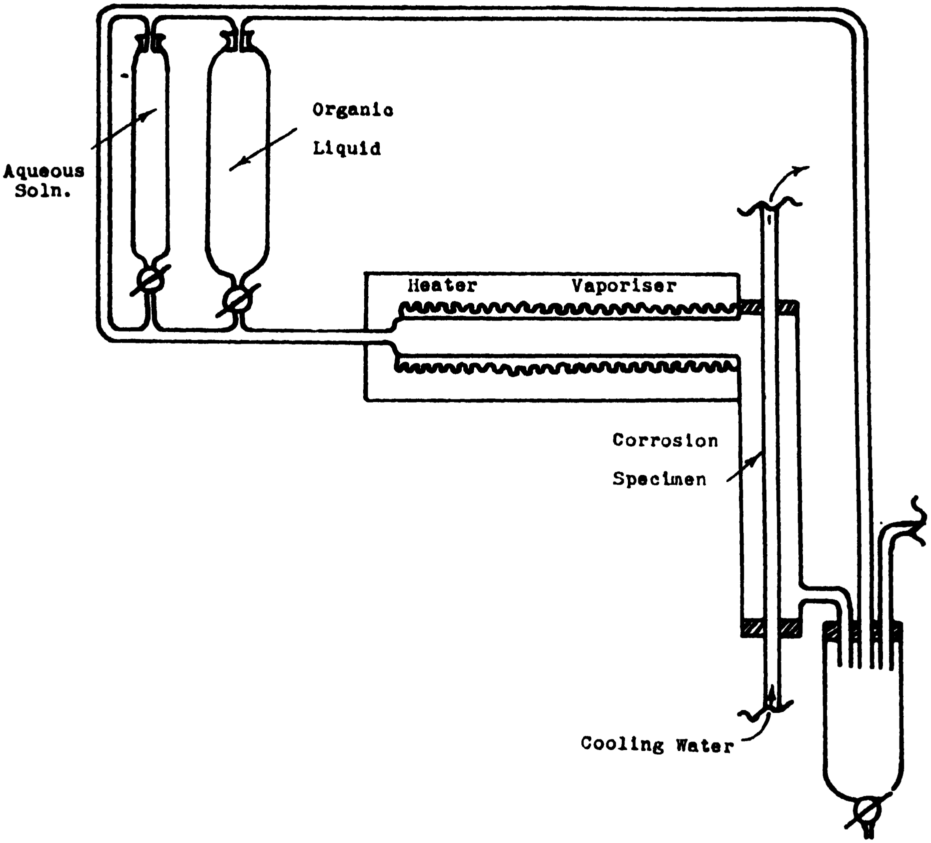


FIG. II-10.—CORROSION UNDER CONDENSATION CONDITIONS.
(After Wachter & Tresider, *Chem. Eng. Prog.*, 1947)

chemical plants handling volatile chemicals or dust-forming solids very wide diversities exist and the spray test should be adjusted to fit the probable circumstances. In accepting figures shown for paint coatings, it must be remembered that a small strip of clean metal is very easily protected by any paint with a reasonable adhesion. A very different result can be obtained if the same paint is applied to steel or other metal work which had been exposed to the weather before painting—a point that is further discussed in Chapter XII. Some doubt has also been expressed as to whether accelerated ageing tests do give results of a satisfactory nature for paint films, even when the specimens are so prepared as to expose all likely positions to the spray effects.

Rapid flow of liquid over a solid surface can give rise to both erosion and potential difference, as indicated in the previous chapter, while when air is present the increased supply of oxygen may either stimulate or check corrosion. If, then, a metal is proposed for pump construction, or any other similar function, a test should be applied to simulate working conditions. The most usual is one of impingement, in which a stream of the corroding liquid strikes the surface of the specimen. Bengough and May[14] described a standard form some years ago, which is still widely used. Attack on marine condenser tubes was being investigated, and a stream of water carrying entrained air passed from a 2-mm. jet to strike an adjacent surface at velocities of the order of 10 feet per second. Jets of air and hydrogen gas, striking the immersed metal, have also been used.

It is often necessary to estimate the protective quality of a coating over a surface. Where this covering is of one metal over another, as in electroplating, the main weakness is the existence of pinholes. A sample of tinplate, with protected edges, immersed in air-saturated hot distilled water (95° C.), will develop rust spots over every pinhole that penetrates to the iron base in less than five hours.[15] This test is more rigorous than immersion in a solution of potassium ferricyanide, which gives blue spots at the failure points. Solutions of this salt, with additions of sodium chloride or sulphuric acid (*c.* 1%), are widely used, however, for tests on all forms of coating on iron. When the coating is on non-ferrous metals, it will normally be possible to find some reagent which will give a suitably coloured product; a chromium deposit on nickel can be tested with ammoniacal dimethyl-glyoxime, yielding pink spots at pinholes.

Paint coatings are not so easy to test as those of metal, which normally fail only by pinhole faults. A paint coating can crack, strip, or transmit corroding agents in many ways, and the only real test is some form of service or field test. Spray testing in a special chamber, combined with exposure to an ultra-violet lamp, has been widely used in an attempt to give accelerated weathering, but it is doubtful if the results are an infallible guide to service life.[16, 23] It is always necessary to test under alternate wet and dry conditions, as the changes in form of the paint film under such treatment are a frequent cause for failure. Lobry de Bruyn,[17] in a discussion of these tests, recommended a cycle of at least an hour's duration to give time for volume changes. Pinholes in a paint film can be detected by the means given for metal plating, choosing a suitable solution for immersion, but many paints will allow sufficient water to diffuse through to lift the paint film locally and so destroy suitable experimental conditions. This penetration is probably responsible for the fact noted by Crennell[18] that painted steel is cathodic to a clean steel surface when both are immersed in sea water.

It is improbable that paint coats will be put under very severe operating conditions as regards abrasion or distortion when used in chemical plant, but tests for these qualities may be mentioned. Abrasion resistance can be measured by a sand blast, with the amount of sand or carborundum powder used to give penetration being used as a measure of resistance.[19] Brittleness can easily be tested by scratching the paint film with a needle point; the brittle film flakes off as a series of small circular discs, while a tough covering shows a straight tear.

STRESS CORROSION

The paragraphs above have dealt with mechanical and chemical tests on materials, but these effects must be combined to deal suitably with estimates of stress corrosion. Tests carried out on small specimens may be quite misleading in that preparation of the test-piece has removed the effects of stress. In the process of wire-drawing, surface layers are very much distorted, but loss of a few molecules in the early stages of corrosive attack will remove this distortion, and further corrosion is normal. If, however, the wire is held under stress by a constant external force comparable with that used in the drawing operation, then actual deformation will persist, and intercrystalline corrosion may be very marked. On the other hand, the stress applied cannot be greater than the elastic limit, and effects of permanent bending, which imply the application of a force in excess of this limit, cannot be studied. Experiments must cover the possible range of conditions to be met with in practice, and no single test will suffice.

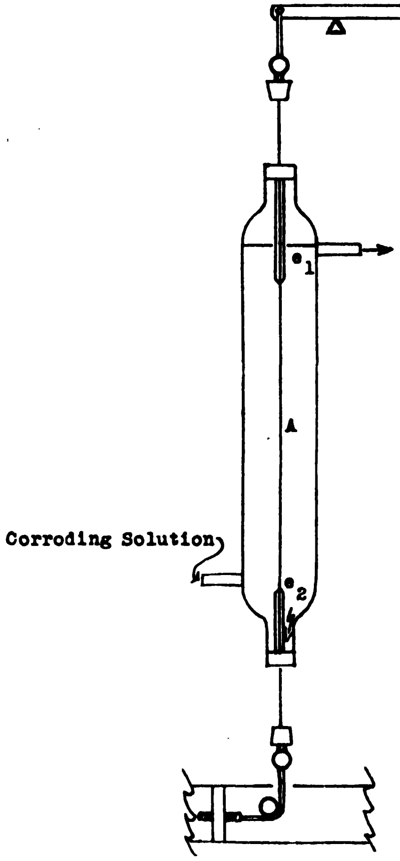


Fig. II-11.—Corrosion Under Stress.

For study of stress approaching the elastic limit, the most typical test apparatus is shown in Fig. II-11. A wire (A) of the metal to be examined is held under constant load by the weight W, while the corroding solution is pumped through the containing vessel at a rate low enough to avoid any question of erosion, but sufficient to maintain reagent concentration constant. It is necessary to sheath the ends of the wire at the points e_1, e_2, or these zones will almost certainly be preferentially attacked. This precaution lends a somewhat artificial air to the test, as almost all stress-corrosion failure in actual practice is by just such preferential attack. Nevertheless the apparatus lends itself to testing of a wide range of reagents at varying temperatures.

While this test will show any tendency of the metal towards failure under conditions of corrosion and load, it is only applicable to fairly thin wires, and not to heavier preformed sections. Small sections of a heavy bar can be bolted into a distorted form, as shown in Fig. II–12*a*, and the whole test-piece immersed. Ideally the bolts should be of the same metal as the two test-bars and central block, but the localised effects of stress corrosion can usually be separated from general electrolytic corrosion. As a test on the effect of greater loads, a specimen can be cold-bent to a permanent set as shown in Fig. II–12*b*, and exposed to corrosion in the ordinary way.

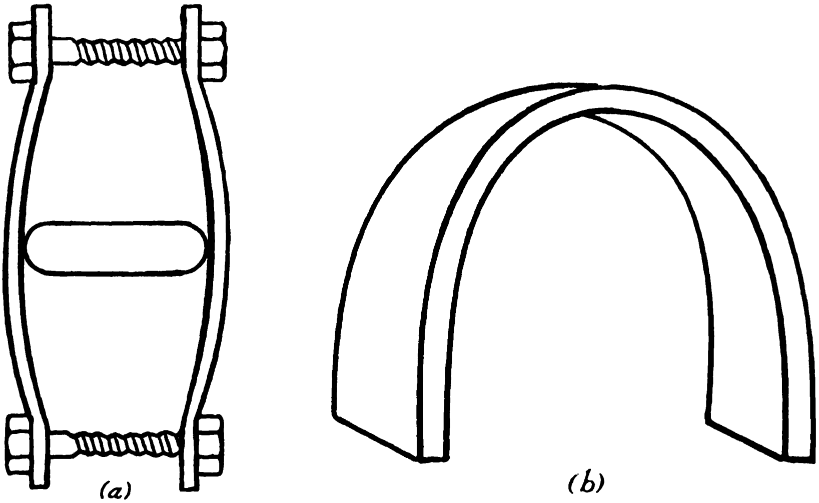


FIG. II–12.—STRESS CORROSION TESTING.

Corrosion fatigue tests are carried out in an ordinary rotating test machine, with the corroding liquid applied to the specimen by some form of wick. Perhaps the best form is that described by Huddle and Evans,[20] in which a wick is stretched by a plastic bow so that it just clears the metal surface (Fig. II–13). Then the liquid reagent, running down the wick, forms a ring contact on the specimen by capillarity.

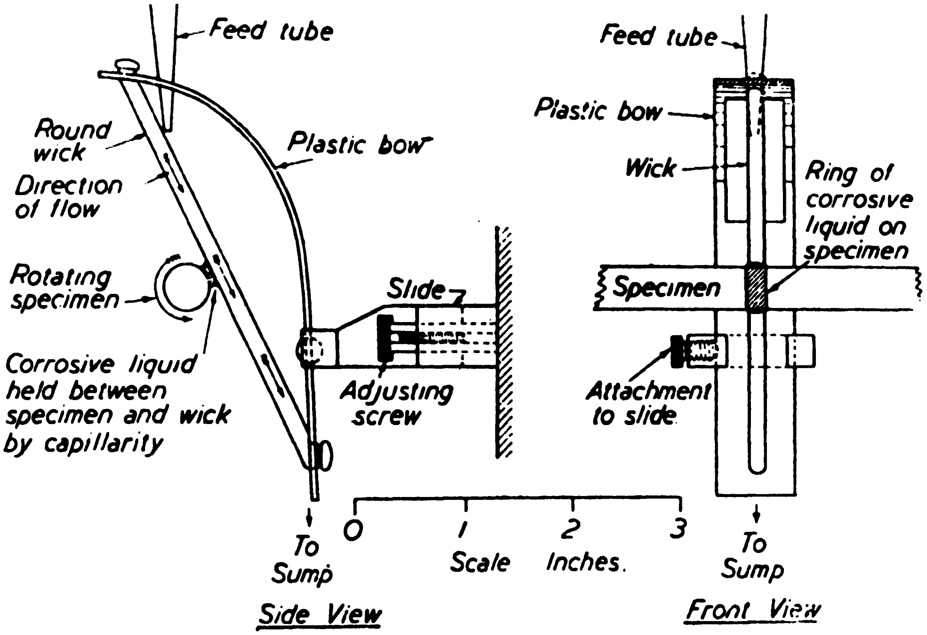

Feed tube
Round wick
Direction of flow
Plastic bow
Rotating specimen
Corrosive liquid held between specimen and wick by capillarity
Slide
Adjusting screw
To Sump
Side View
0
1
2
3
Scale Inches.
Feed tube
Plastic bow
Wick
Ring of corrosive liquid on specimen
Specimen
Attachment to slide
To Sump
Front View

FIG. II–13.—CORROSION FATIGUE TEST.
(Huddle & Evans, *Jl. Iron Steel Inst.*, 1944, 149, 109)

For a general discussion on the methods for testing stress corrosion, reference may be made to the symposium on this subject published by the American Society for Testing Materials in 1945.[21]

REFERENCES

1. British Standard 18 (1950).
2. ,, ,, 1452 (1938).
3. ,, ,, 1257 (1945).
4. ,, ,, 240 (1937).
5. ,, ,, 427 (1931).
6. ,, ,, 891 (1940).
7. Gough, H. J., and Sopwith, D. G., *J. Inst. Met.*, 1932, **49**, 93.
8. Evans, "Metallic Corrosion, etc.", p. 437, *et seq.*
9. Evans, *loc. cit.*, p. 71 *et seq.*, 752.
10. See, e.g., B.S.S. 110 (1949) for Cr-Ni corrosion-resisting steel.
11. Day, C. W., *Chem. Eng.*, 1952, Jan., p. 155.
12. Swinden, T., and Stevenson, W. W., *J. Iron Steel Inst.*, 1940, **142**, 165.
13. Vernon, W. H., *loc. cit.*, 1940, **142**, 183.
14. Bengough, G. D., and May, R., *J. Inst. Met.*, 1924, **32**, 137.

15. Macnaughton, D. J., *et al.*, *J. Iron Steel Inst.*, 1932, **125**, 160.
16. Symposium, Reports, *Chem. and Ind.*, 1952, p. 353.
17. de Bruyn, C. A. L., *Paint Var. Prod. Manf.*, 1935, Mar., p. 16.
18. Crennell, J. T., *J.S.C.I.*, 1950, **69**, 371.
19. Schuh, A. E., and Kern, E. W., *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 72.
20. Huddle, A., and Evans, U. R., *J. Iron Steel Inst.*, 1944, **149**, 109.
21. "Symposium on Stress Corrosion Cracking", A.S.T.M., 1945. See, e.g., p. 233 *et seq.*
22. Wormwell, F., *J. Appl. Chem.*, 1953, **3**, 164.
23. Report on Testing of Paint Films, *J. Iron Steel Inst.*, 1952, **171**, 255.

CHAPTER III

CAST IRON

THE IRON–CARBON SYSTEM

In order to form any clear idea of the nature both of cast iron and of steels, it is necessary to consider the equilibrium between elemental iron and carbon. Iron itself, in pure form, has two distinct allotropic forms, α (alpha) and γ (gamma) irons. The cooling curve of a pure metal, solidifying at 1535° C., shows breaks at 1400°, 910°, and 768°. These suggest four solid phases, which were originally known as α, β (beta), γ and δ (delta) irons. It is now generally agreed that the stable low-temperature α phase, though losing its magnetic properties at 768°, does not change in essential structure, so that the β form is a modified α iron. γ iron, stable between 910° and 1400° C., has a different crystal structure from the α form, and widely different solvent action on carbon and other alloying elements. The high-temperature δ iron, stable between 1400° and the melting-point of the metal, has the same crystal structure as the α modification, and there is no reason to suppose that it forms a special phase. Pure iron, then, is stable as the α phase from ordinary temperatures to 910°, and again from 1400° up to 1535°, while the γ phase is stable only between 910° and 1400°. Phase changes are comparatively slow, especially as the temperature of the metal falls, and it is general to find both forms persisting outside their legitimate temperature range.

When other elements are added to the pure metal, the general effect is to change the temperature range in which the γ iron is stable, while a secondary action is the acceleration or slowing down of phase-change rates. Silicon restricts the temperature range very sharply, and for a content of more than 3% prevents γ formation completely. This alteration produces a so-called "γ loop" in the iron–silicon diagram, as shown in Fig. III–1. On the other hand, nickel increases the temperature range (Fig. III–2) and it is difficult to obtain nickel alloys of more than 10% of nickel in an α-iron form. Almost all alloying elements diminish the rate at which γ iron changes to the α form, even though the final equilibrium is unaffected. Manganese alloys containing some 10% of Mn can easily be obtained in an "austenitic" form, as the gamma-iron phase is usually called. When put under any form of stress, they toughen and "work-harden" to an abnormal degree owing to the formation of complex α iron or "ferritic" phases.

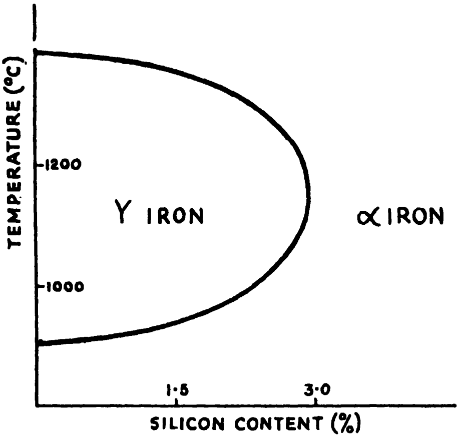


FIG. III-1.—IRON-SILICON DIAGRAM.

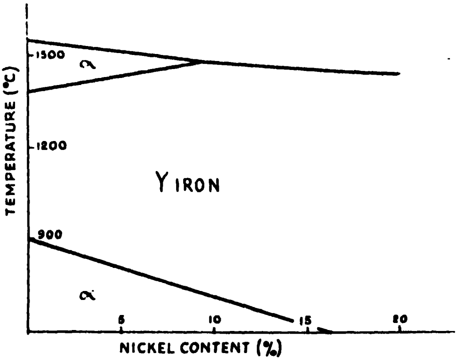


FIG. III-2.—IRON-NICKEL DIAGRAM.

Carbon, the most important property-determining element added to iron, is similar to silicon in its effect on the "γ loop", as shown in Fig. III-3. This diagram sets out the whole range of mixtures in which a stable solid compound of carbon and iron can exist. The upper limit for carbon is given by the composition of Fe_3C, iron carbide or "cementite". This hard, brittle alloy does not form any solid solution with its constituent elements, and no compound richer in carbon is known to exist. The composition of cementite corresponds to 6·7% of carbon, and all liquid mixtures containing between 4·3% and this higher figure will deposit Fe_3C as solid phase on cooling. Then the composition of the liquid mix will approach that shown by the point B (eutectic) as the temperature falls, and finally the residue will solidify as a whole at the eutectic composition. The solid so formed, with 48% of "austenite" and 52% of "cementite", is known as "ledeburite".

On the other side of the eutectic, with less than 4·3% of carbon, molten mixtures deposit "austenite"—a solid solution of carbon in γ iron, except for the low-carbon group (less than 0·5% C) which pass through a transitory α-iron phase. Again the composition of residual liquid tends to move towards the eutectic, but here the alloy may solidify completely before this end-point is reached. For an alloy having a composition represented by M_1 in Fig. III-4, with 1·5% of carbon, solid-phase formation begins at 1420° C., an austenitic solid separating with composition

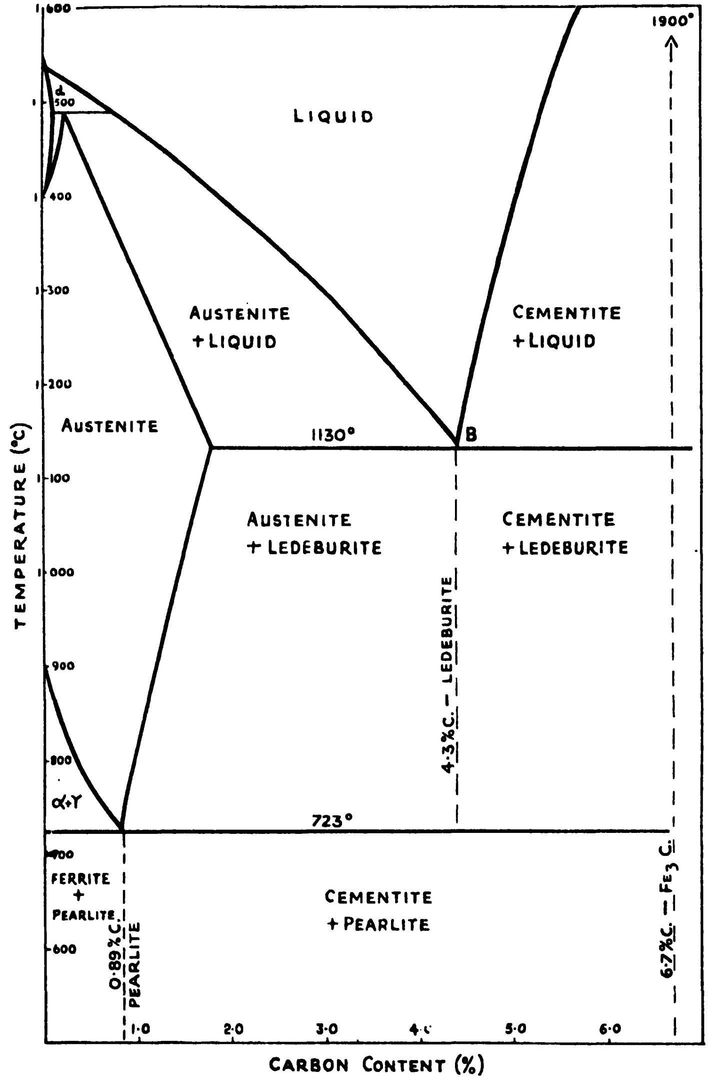

1,600
1,500
1,400
1,300
1,200
1,100
1,000
900
800
700
600
δ
LIQUID
AUSTENITE + LIQUID
CEMENTITE + LIQUID
AUSTENITE
1130°
B
AUSTENITE + LEDEBURITE
CEMENTITE + LEDEBURITE
4·3%C. — LEDEBURITE
α+γ
723°
FERRITE + PEARLITE
0·89%C — PEARLITE
CEMENTITE + PEARLITE
1900°
6·7%C. — Fe₃C.
1·0
2·0
3·0
4·0
5·0
6·0
TEMPERATURE (°C)
CARBON CONTENT (%)

FIG. III-3.—THE IRON-CARBON DIAGRAM.

represented by M_2. As this contains only 0·5% of carbon, the remaining liquid is carbon-enriched, and moves in composition along the line A—B, the "liquidus" curve. Diffusion changes in the solid phase at these temperatures are rapid, and the composition of the austenite moves in sympathy along the line M_2—D, the "solidus" curve. When a point M_3 is reached on the liquidus curve, the last traces of liquid disappear, the final solid containing, of course, the 1·5% carbon content of the original liquid metal. An alloy such as M_4 will start to solidify at 1230°, and the liquid phase will reach eutectic composition with comparatively large amounts still molten. Then the residue will solidify without further change, forming ledeburite together with "primary" austenite. As mentioned above, mixtures containing more than 4·3% of carbon will

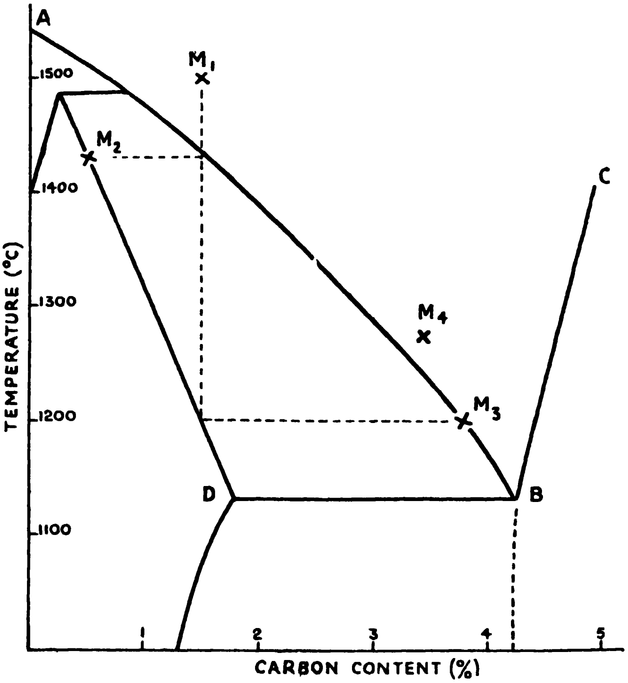


FIG. III–4.—AUSTENITE REGIONS-(FE–C) DIAGRAM.

deposit cementite, but in practice this part of the iron–carbon diagram is of little or no importance.

As will be seen from Fig. III–3, it is only in regions of total carbon content less than 1·7% that austenite can exist as a stable form, with carbon in solution, as a homogeneous solid phase. It is the established practice to define all alloys with less than this 1·7% of carbon as "steels", and all with more carbon as "cast irons" or simply "irons". Alloys containing less than 0·1% were known as "wrought iron", but are now regarded essentially as low-carbon steels. Methods of manufacture produce certain forms of slag inclusion which alter corrosion resistance, but not to any great extent.

The solubility of carbon in γ iron falls steadily as the temperature decreases. Solubility in α iron is very small at any temperature level (as will be seen later). Now all simple iron–carbon steels assume an austenitic form as they solidify and start to cool. This is true even for the special low-carbon steels which have solidified originally to an α phase, for transformation is rapid at high temperatures, and further cooling takes the whole solid into the region of the "γ loop". As cooling continues, the limits of stability of austenite are reached at some point on the lines D—E or E—F of Fig. III–5. For the alloy M_1 with 1·5% of carbon, this stage is reached at 1050° C., and carbon begins to pass out of solution as cementite, leaving a solid residue which is increasingly poorer in carbon, until the point E is reached, with 0·89%. Then the austenite remaining is transformed into a special "eutectoid" mixture of

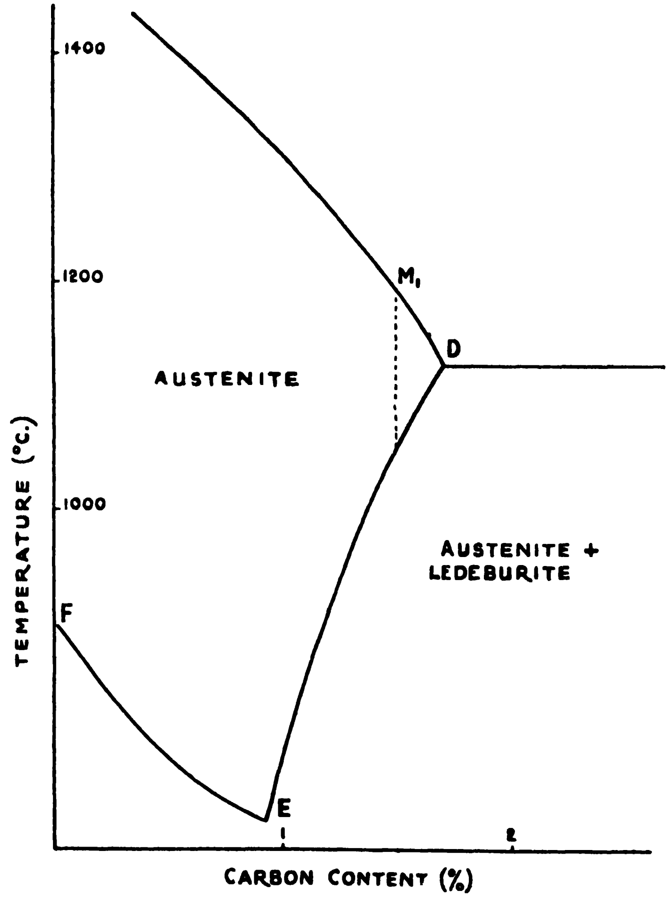


FIG. III–5.

α iron with a trace of carbon—"ferrite"—and cementite. This eutectoid has, like ledeburite, a characteristic crystal structure, and is known as "pearlite". Austenitic alloys containing less than 0·89% of carbon will reject ferrite, along the line F—E, until the eutectoid composition is reached as before.

It is usual to define steels containing less than 0·85% of carbon as "hypo-eutectoid", while those with 0·89 to 1·7% are "hyper-eutectoid". Similarly the irons of 1·7 to 4·3% carbon are hypo-eutectic, and those of more than 4·3% hyper-eutectic. Again, the solid phase formed before the final eutectic/eutectoid composition is reached is designated "pro-eutectic" or "pro-eutectoid". Then a steel containing 0·5% C will form pro-eutectoid ferrite and pearlite, while a cast-iron mixture containing 3% of combined carbon will harden initially to pro-eutectic austenite and ledeburite. As cooling of this last mixture proceeds, the austenite phase rejects carbon in the form of cementite, corresponding to the drop in solubility from 1·7 to 0·89%. At 723°, the austenite becomes unstable, and is gradually converted into pearlite. Another phenomenon is superimposed on these changes—the gradual formation of carbon and ferrite from cementite. This graphitisation of cast iron can take place at all temperatures, and can be accelerated by various additions of other elements. All commercial cast irons will contain free graphite, either as coarse flakes, finer particles, or "nodules".

THE SOLID STRUCTURE OF CAST IRON

It is not necessary to consider any of the hyper-eutectic irons containing more than 4·3% of carbon, as these are never used in normal practice. Commercial cast iron will have a carbon content which can vary over the whole possible range, but this carbon will be present as graphite, as cementite, and in solid solution associated with either α or γ iron. As the total content rises, more and more carbon separates as graphite, but if the iron is relatively free from other elements the bulk is still retained in combination. The most common impurity in any ordinary iron is silicon, produced by partial reduction of slag, and this element markedly promotes the formation of graphite. At the same time, rapid chilling of a molten metal, to temperatures below those at which any phase changes are likely to occur, may hold carbon in a combined form.

It follows, then, that the relative amounts of free and combined carbon are determined by the previous thermal history and by the silicon content, with other elements as a rule playing some minor part. A casting in which certain sections have been cooled rapidly will retain much more carbon in combined form than is present in the slower-cooling portions. Most castings will originally have a more or less "chilled" surface, consisting largely of cementite and pearlite, even though the interior is mainly of graphite and ferrite. These two varieties of cast iron are known as "white" and "grey" from their general appearance. Pearlitic white iron is very hard, and an entire casting in this form will be too brittle for ordinary use. Grey cast iron, with a ferrite structure, is tough enough for all ordinary purposes, with good machining qualities, but the graphite flakes act as a nucleus for corrosion cells. The characteristic solid

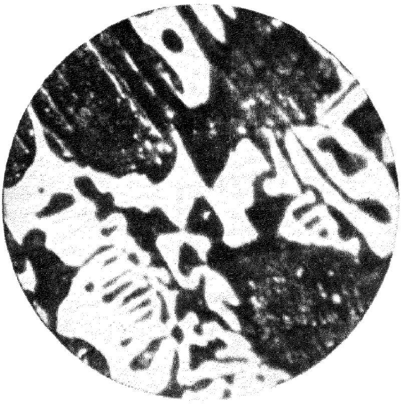


FIG. III-6.—WHITE CAST IRON. CEMENTITE (LIGHT), PEARLITE (DARK).

(From Woodward, *Engineering Metallurgy*)

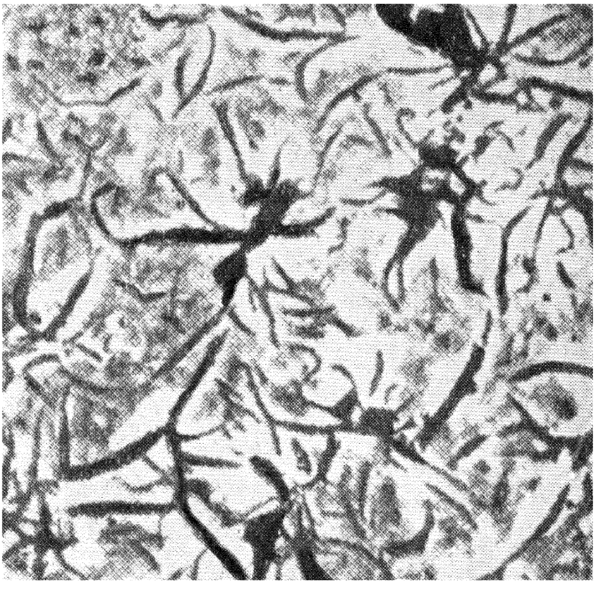


FIG. III-7.—GREY CAST IRON, SHOWING COARSE GRAPHITE.

(*Courtesy of J. G. Pearce, Proc. Chem. Eng. Grp.*, 1948) phases of these cast irons can be seen easily in micro-photographs of polished and etched surfaces. A chilled white iron is shown in Fig. III–6, while a rather poor specimen of grey iron, having large graphite flakes, is shown in Fig. III–7. The ideal grey cast iron should have the graphite evenly dispersed in fine flakes or nuclei, as shown in Fig. III–8. This last structure can be obtained by setting the carbon content at about 3·5%, with some 1% of silicon in the melt. Just before casting a further 2% of silicon is added as a fine powder of ferro-silicon or calcium silicide. If about 0·1% of cerium is added at the same time, the deposited graphite forms nodules rather than flakes. Fig. III–9, described by J. G. Pearce,[1] shows this effect very clearly. It is now general, for all chemical plant construction, to specify a "high-duty" iron casting, as these finer-quality irons are known from their improved mechanical qualities. From a chemical standpoint, however, their use is based upon increased resistance to all corrosive influences. Large graphitic inclusions form an ideal cathodic area, while opening fine cracks along the grain boundaries to the entrance of oxygen or steam. The

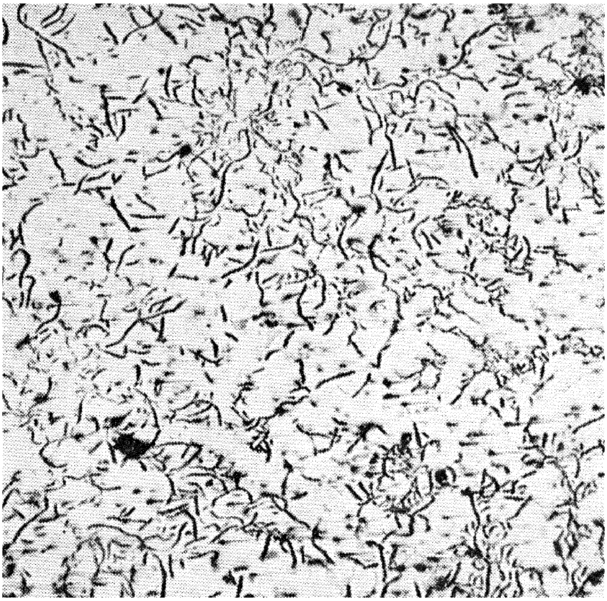


FIG. III–8.—GREY CAST IRON, SHOWING FINE GRAPHITE.
(*Courtesy of Dr. J. McLeod, Metallurgy Dept., Royal Technical College, Glasgow*)

"growth" of cast iron at elevated temperatures, referred to below, is almost certainly due to penetration of this kind. Where the carbon fragments are small or rounded, both these effects—penetration and cathode formation—are greatly diminished.

While silicon is the most effective agent in promoting graphite formation, nickel acts in the same way and is sometimes preferred in that it has only slight effects on the pearlitic complex. A cast iron with 1% silicon and 2% of nickel has a pearlitic structure with little or no unassociated cementite, while the graphite is still in a fine flake form. This nickel-bearing iron has the advantage of consistent structure, though the time of cooling may vary. A casting of normal cast iron with 2% silicon will tend to give a coarse graphite structure in thicker and more slowly cooled parts. If the silicon is reduced to prevent this, then a chilled white iron will be formed at the thinner sections of the casting. If the nickel content of the melt is still further increased to about 4–5%, it will stabilise the austenitic γ iron formed on initial solidification. The rapid cooling characteristic of all casting will then produce a special type of iron structure known as "martensitic". Martensite is more

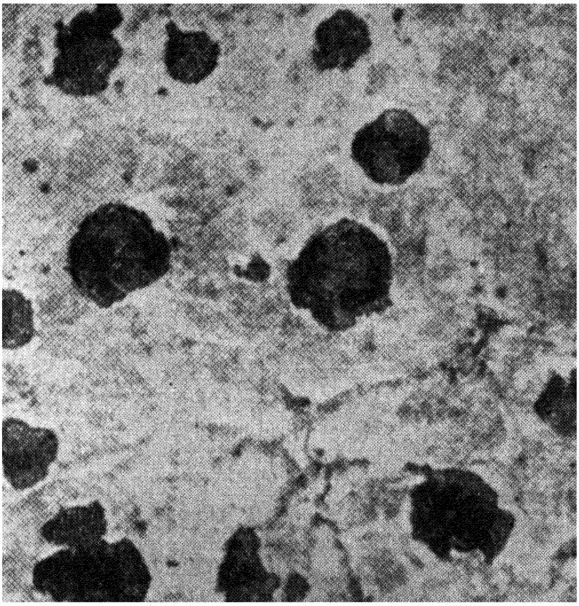


Fig. III–9.—Grey Cast Iron, as Fig. III–7 after Nodulising Treatment.
(Courtesy of J. G. Pearce, Proc. Chem. Eng. Grp., 1948)

important in steel-working than in casting, but it is essentially a homogeneous solid solution of carbon in iron, crystallising in needles, as shown in Fig. III–10. Still larger amounts of nickel can stabilise the austenitic form completely, but these high-alloy mixtures are too costly for general use, and will be dealt with in a later chapter.

Chromium is a most effective agent in checking graphitisation, and can be used to offset the effect of silicon. Unfortunately, it tends to come out of solution as a hard carbide, though any residual graphite is deposited as a fine flake. A combination of 3% Ni and 1% Cr produces finished castings with a stable pearlitic matrix, holding a very fine graphite grain. Copper also functions to give a fine graphite, and has the advantage of increasing fluidity in the melt when added in quantities up to about 1·5%.

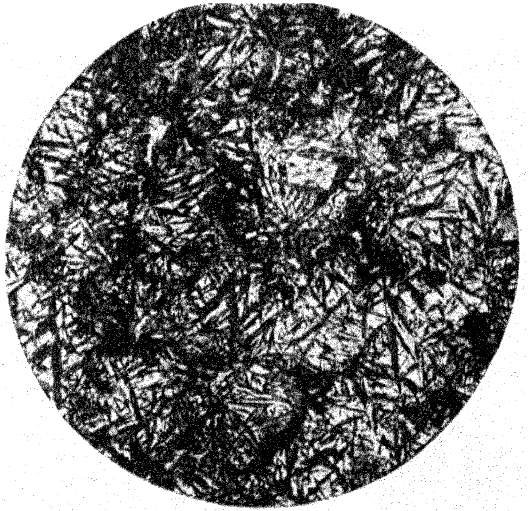


FIG. III–10.—MARTENSITIC CAST IRON.
(From "Metallurgical Materials". *Courtesy of V. N. Wood and Messrs. Chapman & Hall, Ltd.*)

IMPURITIES IN CAST IRON

The term is used in the sense of "undesirable constituents", in that anything but iron and carbon can be held as foreign components. Sulphur is the most undesirable element, even though it stabilises cementite. A low-melting ferrous sulphide appears in segregated form at grain boundaries, and will give outstanding brittleness even in the cold casting, while crack formation during the actual casting process is greatly increased. All good cast irons must have a sulphur content of below 0·1%. High-sulphur-bearing ores are always smelted with a strongly basic slag to cut down the amount present in the pig iron, but the final elimination is generally carried out by the addition of manganese. This forms an insoluble sulphide, MnS, and the manganese content is adjusted to give an excess of about 0·2% above that required for elimination of sulphur. The slight excess checks graphite formation, but manganese is not very active in this way, and is seldom used in quantities above those required for sulphur removal.

Phosphorus is not quite so harmful as sulphur, but it, too, forms a very low-melting eutectic, containing a characteristic iron phosphide, Fe_3P. This does not appear to segregate so completely as the sulphur compound, and addition of phosphorus has in fact been deliberately practised to give a very fluid melt for light castings. These are mainly used for ornamental work, or for cheap mass-production of drainpipes and similar articles. As 1% of phosphorus represents some 10% of the finished mixture, large inclusions of the low-melting eutectic can appear at the centre of heavy sections, representing a possible weakness that cannot be detected by test-pieces. A chemical cast iron should not have a phosphorus content much in excess of 0·2%, and the composition of the casting mix must be adjusted accordingly. If high fluidity is required, it should be produced by the addition of copper.

Apart from these two elements, no ordinary constituent of cast iron can be held as altogether harmful. Silicon in excess of the amount required for graphite production gives a weak and brittle structure to the residual ferrite, while many alloying metals in excess can produce undesirable reactions. Normally, they would need to be deliberately added at considerable cost, and it is hardly likely that such mixtures will be met with in ordinary casting metal.

MECHANICAL PROPERTIES OF CAST IRON

The range of properties to be expected from a standard cast iron have been laid down in British Standards,[2] the latest being B.S. 1452 (1948). Regulations are laid down for a tensile strength test and for a transverse rupture stress on a loaded bar. Seven grades of iron are postulated, with steadily increasing strength and costliness. The ultimate tensile strength increases from 11 to 28 tons/sq. in., while the rupture test shows a similar change from 20·5 to 42 tons. Values for the deflection before breakage in this rupture are also specified. No general rule is laid down for hardness, and it would seem that all normal impact tests are too severe for castings, though a special test with an unnotched bar has been suggested.[3] The fatigue limit of a good grey cast iron is about half of the normal ultimate strength, while the effect of temperature begins to be notable at about 400° C. Normal cast iron should not be put under stress at any temperature above 500° C. The specific gravity varies from 7·1 to 7·2 (0·258–0·261 lb./cu. in.), and the thermal conductivity from 27 to 29 B.Th.U./(sq. ft.) (hr.) (° F. per ft.), both measured at ordinary room temperatures.

CAST-IRON COMPOSITIONS

While no standard composition ensuring the mechanical properties set out above has been set up, certain mixtures have been shown to exhibit suitable characteristics. Precise figures will vary from one manufacturer to another, but the range shown in Table III–1 below will cover most of the typical usages in chemical plant.

TABLE III–1

Carbon		Si	P	S	Mn	Ni	Cr	Usage
Total	Combined							
3·2	0·5	2·5	0·6	0·1	0·7	—	—	Sulphuric-acid concentration.
3·6	1·5	1·5	0·04	0·06	0·75	—	—	Caustic-soda fusion.
3·0	0·8	1·8	0·2	0·06	0·8	—	—	High-duty pump casings.
3·0	2·8	0·5	0·4	0·15	0·9	—	—	White-iron grinding parts.
3·5	0·8	—	—	—	0·4	2·5	1·5	Martensitic ball-mill lining.
2·9	—	1·5	—	—	0·8	1·5	—	High-duty Ni-iron, "Ni-Tensyl"
3·3	—	1·2	—	—	0·8	3·0	0·5	Good machining qualities.
3·0	—	1·5	<0·08	<0·08	0·8	2·0	—	Heavy pot castings.
3·5	—	0·5	Cu 2·5	—	—	—	0·25	Good corrosion resistance.

FABRICATION OF CAST-IRON PLANT

In the process of casting a mould is normally made up from foundry sand and water, cemented by traces of some adhesive.

Such a mould structure is weak and complicated forms are not self-supporting. As an alternative to sand, loam—a mixture of sand and clay—can be used to form the mould. This is slightly stronger, but the process is a little more expensive. Both loam and sand moulds are brushed over with a suspension of carbon in water—blackwash—to prevent the molten metal from sticking to the mould. If the blackwashing has been carelessly done, some of the moulding material will disintegrate and pass into the casting, leaving a rough patch on the cooled metal surface and a possible centre for corrosion below. Any casting with local bulges and a roughened surface will normally be rejected by the founders, but a further inspection is always worth while.

A complicated form will always need supporting wires or tie-bars to fix the foundry cores into place. These metal supports will be covered by molten metal and left in the finished casting. They will be of a different form from the surrounding metal, and can act as a centre of corrosion. Pump valve-seats or stirrer brackets are particularly liable to suffer in this way. The obvious remedy is to design a chemical plant casting so that it needs no supported cores, but this may not always be a practicable proposition. An ideal form for moulding would be a cylinder, open at both ends, or a hemisphere cast with the curved surface upwards. The walls should be of even thickness and there should be no sharp corners or changes in cross-section. If possible, the original chilled skin of white iron over a softer and tougher core should be preserved for its corrosion-resistant qualities. This suggests that after-machining should be eliminated wherever possible.

The design of any cast-iron plant should always be considered with these aspects in mind, as well as the more customary factors of casting weight, shrinkage, and adequate strength. Fortunately it is never necessary to make rectangular tanks in a single casting, but all corners should be curved to a generous radius, while flanges should not be widely different in thickness from the carrying walls. The typical cast-iron reaction vessel used in many chemical plants is shown in Fig. III–11. For this diagram it is shown connected up as a sulphuric acid pot concentrator, with the primary acid cooler at the side. This is also in cast iron, and shows how severe the conditions may be for such plant. The acid flowing into the cooler will be at nearly 300° C., and the centre section of the cooler has sometimes been made of silicon iron (Chapter X). All parts are of even thickness, with a slight thickening towards the heavier flanges. Openings in the lid which call for machining are all arranged at the same horizontal level, so that a single set on a surfacing machine will allow the cutting of all flange fittings. The flanges are often cast with slots for the bolts to avoid drilling and local destruction of a surface metal. It is not desirable, however, to cast these vessels in the easiest way—flange downwards on a prepared metal plate—which gives a chilled flange surface. Any refuse in the metal will float to the highest point in the casting, in this case the middle of the curved bottom. If cast in this way, it is necessary to allow a very generous "riser", as pipes leading to the mould are called, so that all slag inclusion will float out of the pot metal proper. A still better method is to cast with the flange uppermost, when the soundest metal forms at the corrosion-resistant base, and carry risers up from the flange to remove the slag. Metal fillets to support the mould will now be needed, and these should be made from a cast metal with composition as near as possible to the metal being poured. A discussion on cast-iron chemical plant by Bewsher [3a] raises other design questions and may be consulted with advantage.

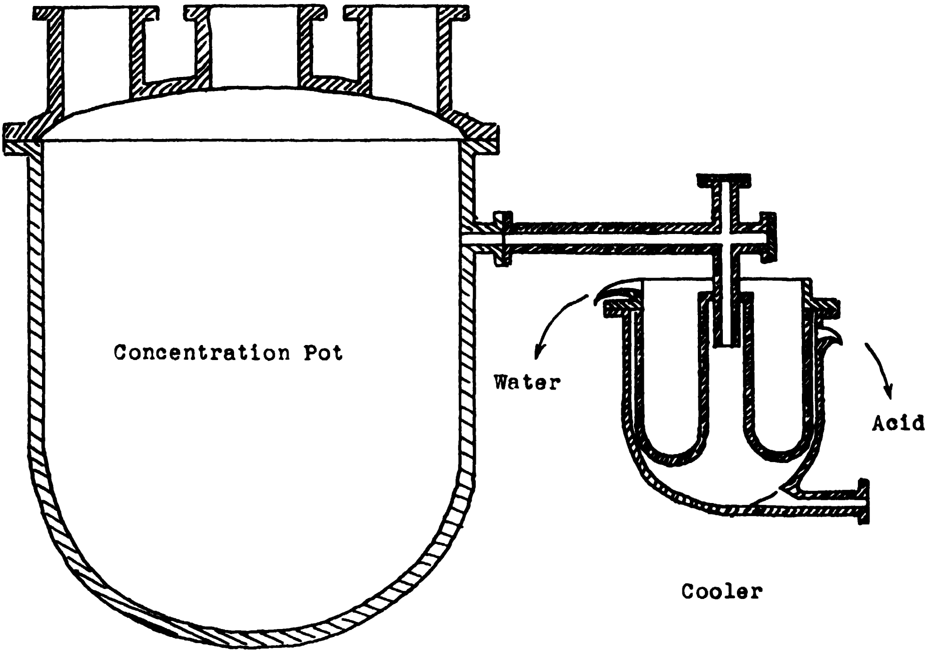


FIG. III–11.—CAST IRON CONSTRUCTION.

A cast-iron shape is generally much heavier than a steel vessel for similar duty. This is not on account of the lower strength of the iron, but because it is almost impossible to secure a really sound casting in normal metal with a wall thickness of less than about $\frac{1}{3}$ in. This is a good fault in some ways, in that a substantial thickness of metal to withstand pitting corrosion is obtained. The rising price of iron in any form, however, is tending to favour the lighter steel, and also other means than sheer weight of metal to check corrosion.

The finished grey cast iron can be machined, drilled, tapped, and planed by all the normal processes of mechanical technology. If heavy machining is intended, then chilled sections should be avoided, and the finished casting can even be tempered to give a uniform ferritic structure. The special nickel irons, giving a martensitic chilled form, are converted to an "acicular" form of ferrite by annealing at 300°–500° C., but ordinary cast irons are heated to a uniform level of 800°–850°, and then cooled over three to four hours. The Brinell hardness, which might have been as high as 350, is reduced to 150, an easy machining figure. For corrosion resistance it is better, as stated above, to leave a homogeneous, slightly chilled surface untouched.

It is possible to weld broken cast-iron sections, or to build up a vessel by welding, using either electric-arc or oxy-acetylene methods, but the weld will always tend to form a chilled section as it cools. The process can be improved by heating up the entire casting to about 700°, and the ease with which carbon can be picked up from incautiously used acetylene has led to the general adoption of an electric arc. Again, a mould can be built up round a damaged section and fresh metal melted into the break by heavy electric currents. Generally the joint is not very sound, and it is probably better to discard a cracked vessel, except in an emergency. Even if this emergency does arise, it will be quicker and probably almost as satisfactory to patch the crack up with a "rust" cement made from iron filings, ammonium chloride and sulphur or manganese dioxide. A mixture of 30 parts filings, 10 sulphur, 2 NH_4Cl, and 20 Portland cement, made to a stiff paste with water, will set over two hours and harden subsequently to a tough resistant bond. A similar mixture has been used as a joint in spigot and faucet joints of cast-iron pipes. The Metalock process, a form of metal stitching, has been recommended for casting repairs *in situ*.[4]

Cast-iron pipes, sometimes in very large sizes, have been and are widely used for drainage, gas mains, and water transport. The individual sections may be up to 20 ft. in length, and the spigoted joints allow the main to be carried round curves or over rock slopes in bends of reasonable radius. The joints are set in place and preformed lead rings or lead wool rammed into position to fill the annular space between spigot and faucet. Alternatively, a ring of greased rope is rammed into the base, and molten lead is poured on top. A better joint than either can be obtained (at an increased cost) by fitting a screwed gland ring which forces down a rubber gasket. Such a joint will stand deflection through 5° of arc without leaking under a pressure of 20 lb./sq. in.

A cast-iron joint must always have some flexibility, especially where flanged joints are concerned. A cast flange is very rigid, and will not deform to make a tight joint when slightly out of alignment. Any attempt to pull up such a pair of flanges on a thin hard gasket will tend to break the flanges at the bolt holes—a remarkably easy feat to any enthusiastic fitter. Cast-iron vessels are never called on for very high-pressure work, and it is comparatively easy to make low-pressure joints tight with a thick soft gasket. When two sections move inside each other with a close fit, as in a gland, care must be taken to see that they are properly aligned before screwing down any tightening nuts. The author remembers vividly a cracked gland on an ammonia plant which cleared a large building very quickly and kept it clear for several hours.

COST OF CAST-IRON PLANT

Cast iron is probably the cheapest form of metal plant construction, though welded steel runs it very close. There is hardly any limit to the size of a single casting, but it must be handled subsequently by machine tools. This sets a normal practical limit at some 15 feet of diameter, though a single pump casing about 25 ft. across was shown at the Glasgow Exhibition of 1951. Probably very large plant could be built up more cheaply in sections with machined flanges. The cost, based on weight, will follow the normal rule that small plant costs more than large, weight for weight, while machining and complicated mould fabrication must be paid for. At the present time (June 1952) it is estimated that simple light castings will cost from £3 to £4 per cwt. in the size range from 1 to 5 cwt., decreasing to £2 to £3 per cwt. as the weight increases to 1 ton. Machining of flanges and joints may almost double this basic figure, while complications in the castings have the same effect. If a special chemical composition is called for, prices will naturally reflect the cost of the ingredients.

These figures are the first suggested costs in the book, and at this point it must be stressed that all costs are primarily labour costs and really represent man-hours in a final analysis. The curves of Fig. III–12 illustrate the position as it existed up till the period 1945–50, and show how fugitive money values can be. In such circumstances all cost figures quoted in the following pages can only be taken as comparative one with another and accepted even then with considerable mental reserve. On the day these words were written (June 15th, 1952) an increase in the price of copper from £231 to £281 was announced, while natural rubber world prices had *fallen* by some 50% in the preceding six months.

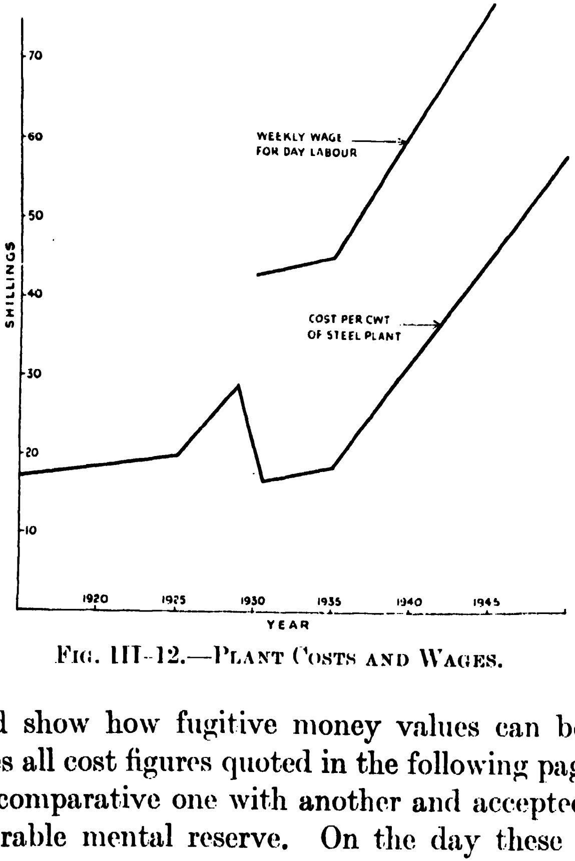


FIG. III–12.—PLANT COSTS AND WAGES.

CORROSION

Atmospheric and Aqueous Attack

Although cast iron has certain specific characteristics in this respect as compared to steel or wrought iron, all three forms behave very similarly in most normal circumstances. As the largest bulk of all commercial plant is made up from these materials, it is of the utmost importance to follow and check ferrous metal corrosion in every possible way. The normal method by which iron corrodes in freely aerated water, or in moisture-laden atmospheres, is by the absorption of oxygen at local cathodes and the corresponding formation of ferrous ions at anodic areas.

(1) $O_2 + 2H_2O + 4e \rightarrow 4OH'$ (2) $2Fe$ (Metal) $\rightarrow 2Fe^{++}$

This is followed, in neutral solutions, by formation and precipitation of ferrous hydroxide, or by oxidation and precipitation of the still less soluble hydrated ferric oxide.

$$(3)\ 2Fe^{++} + 4(OH)' \rightarrow 2Fe(OH)_2$$

$$(4)\ 2Fe(OH)_2 + O_2 \rightarrow Fe_2O_3 . H_2O$$

Either of these precipitates can blanket off the active areas and check reaction, but their effectiveness in this respect depends upon the way in which precipitation occurs. As the OH^- ions have, to some extent, to migrate from the cathodic area, a precipitate of $Fe(OH)_2$ will normally be formed at a little distance from the anodic surface, and corrosion will continue. This effect will be accentuated by the presence of some dissolved oxygen diffusing from the water surface, and meeting ferrous hydroxide in solution. The less soluble hydrated ferric oxide will be formed as a loose precipitate, and will prevent formation of the lower hydroxide in solid form. If still more oxygen is present, however, the oxidation can take place immediately at the metal surface, a skin of $FeO(OH)$ forms over the anode, and reaction is checked. Mears and Evans,[5] in a series of tests in varying atmospheres, showed that as the percentage of oxygen in the gas increased, the amount of corrosion steadily decreased in accordance with the above mechanism.

In the corrosion of a moistened iron surface exposed to air, the anodic and cathodic areas are generally quite close to each other, and a skin of firm rust is soon formed, below which corrosion is slow unless disturbing influences are present. On the other hand, if a large tank is partly filled with water, diffusion of oxygen from the water surface is slow, and the iron below the water passes steadily into solution as ferrous ions, which reprecipitate as hydroxide some little way from the anodic area. The main check to corrosion is the rate at which hydrogen ions can be removed at the aerated cathode and no effective anodic film is ever formed.

An iron surface is, in practice, never homogeneous. Cast iron will always contain inclusions of carbon or iron carbide, even if the metal has not been partly covered by an oxide skin during fabrication. This means that initial attack will certainly be concentrated in the more active areas, which may still further accentuate the differential aeration. A rust deposit will be formed first over the areas producing most metal ions, screening the reactive spots from oxygen, but not from ionic migration. The ferrous ions pass through the skin and meet oxygenated conditions, when a further precipitate is formed. Meanwhile, below this deposit, removal of OH^- ions leads to acid conditions in which still more metal passes into solution, and a pit is formed below a "tubercle" of rust. A corroded iron surface below a neutral or slightly acid water always exhibits these characteristic tubercles, which can be scraped away to reveal a more or less concentrated pitted area. The danger of this form of attack is twofold, in that the pitting will sooner or later perforate the metal, while the bulk of the tubercle, anchored to the metal wall, can seriously obstruct fluid flow. It is common to encounter iron pipes which have been almost blocked up by these rust masses, in which the volume of the corrosion product is more than 20 times as great as the volume of metal destroyed. Oil droplets are often the cause for initial formation of a corrosion pit, as the surface below the oil film is unaerated, but probably the most common initiator is a crack or break in the oxide film formed in fabrication. When the encrustation of hydrated oxide grows thick enough, it may prevent metal ions from passing outwards, and corrosion reactions die away. One of the advantages of cast iron over steel for pipes is that the casting is usually much thicker than the rolled steel, and sufficient metal is available for this final checking to take place.

An even iron surface, with no breaks or heterogenities, would not be so liable to this form of attack, and it can be demonstrated that a pure soft iron is less liable to attack than ordinary cast iron or steel. The point is of only theoretical interest, as all commercial irons contain an abundance of solid phases. Unless some protective agent is present, most natural waters will set up this form of corrosion in feebly aerated conditions, and many dissolved salts will accentuate the attack. Chlorides are the most potent, setting up a corrosion cell which may be represented as in Fig. III-13. Inside the tubercle, iron passes into solution, forming the very soluble ferrous chloride, while at cathodic areas outside, oxygen is taken up to form free NaOH. The two salts react at the tubercle skin, precipitating more hydroxide, and liberating sodium chloride in ionised form. The chloride ions can diffuse through the rust to continue the corrosion cycle.

When the iron surface and the liquid are in relative motion, ferrous ions will be swept away, but oxygen in solution is brought into more intimate contact with all areas of the surface. Under neutral conditions, the aeration effect is usually more important, and the effective solution potential of the iron is lowered. The moving parts of an iron pump will be cathodic to the stationary iron shell, and plant which is in continual use may not suffer so much from localised corrosion as idle vessels or pipe-lines.[24] The excess of aeration effects over ionic erosion is peculiar to iron, and copper exhibits the opposite phenomenon.

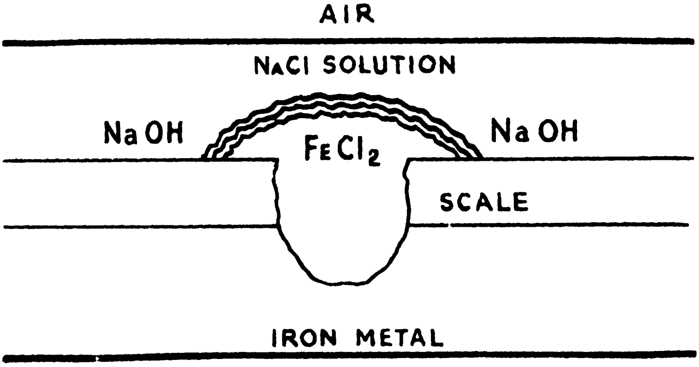


FIG. III-13.—CORROSION PITTING.

Atmospheric corrosion of iron at ordinary temperatures is only possible when liquid water is present. This liquid phase can be formed from moist air by direct condensation on the metal surface, or by capillary attraction in the minute spaces below dust particles. Obviously the air must have more than a certain critical humidity if such condensation is to take place. This critical value is normally about 60%, but can be lowered by the presence of acid gases, notably SO_2, and by the nature of solid dust particles. Simple exclusion of dust cuts down the rusting of a smooth iron surface to a negligible extent if acid gases are not present, even though the critical humidity is largely exceeded. Again, the nature of the dust particles is of considerable importance, as shown by Vernon,[6] who classified dusts into active or inactive forms. Salts, such as ammonium sulphate, were essentially active, while silica dust was relatively inert. Traces of hygroscopic salts left on an iron surface will cause rusting at humidities well below the normal critical value, while rust itself, when once formed, seems to attract moisture and catalyses further corrosion. It has been said, in fact, that rusting, once started, spreads over the metal surface like a "contagious skin disease". In the climate of this country, humidity is usually above the critical figure, while either SO_2 from industry or chlorides from sea spray are present in sufficient quantities to catalyse rusting. Unprotected iron surfaces will therefore rust steadily with rates of attack which may vary from 10 to 50 mdd, as determined by the exact surface conditions of the iron and the circumstances of exposure. Cast iron is usually considered to rust slightly faster than wrought iron, but more slowly than mild steel, but it is very difficult to avoid the effect of slight changes in conditions, and no certain order can be established. Traces of impurity from the original iron ore may often have considerable effect. Thus a copper content of 0·1 to 0·2% has been claimed[7] to diminish rates of attack by over 50% in some cases. J. C. Hudson[8] has estimated the life of 18-gauge sheet (0·048 in.) in ordinary industrial atmospheres as 10 years for mild steel, 12 years for a copper-bearing steel, 13 years for wrought iron, 16 years for steel with 1% chromium and 0·5% copper, 70 years for zinc, and 16,000 years for an 18/8 stainless steel. The shortest life would correspond to a rate of attack of about 24 mdd, but as no exact definition can be given of working life, such figures can only be taken as a general indication. A ½-in. cast-iron section would, on the same basis, be good for about 100 years, and it is interesting to note that the author saw some years ago a cast-iron tank being dismantled after fifty years of use as the base of an ammonia washer. The sections were rusted from the outside, and though very thin in places, were not completely unusable.

Soil Corrosion

Iron pipes are frequently buried in the ground, and will be attacked by air and moisture in a variety of ways. In general, the corrosion will be proportional to

(*a*) Rate of oxygen diffusion to pipe surface.
(*b*) Amounts of specific electrolytes in the soil.

Ample opportunity will always be present for areas of differential aeration to form, while the varying concentration of electrolytes in soil masses pressed against the metal will give corrosion cells of another pattern. In a waterlogged soil, local patches of high acidity will set up cathodic conditions relative to more basic areas. Fortunately, most soil–water mixtures tend to form a "buffered" system of constant acidity, while the reaction products cannot migrate readily, and their accumulation checks reaction in the normal way. As a result, the corrosion of buried pipes in a well-drained sand or gravel soil is not serious, even though oxygen has fairly free access. Waterlogged clay soils give much more trouble, even though it would appear that air cannot penetrate to the pipe. This corrosion is always traced to the combined effects of sulphate and sulphate-reducing bacteria. Anodic reaction follows the normal lines, but the cathode is depolarised by sulphate reduction under anaerobic conditions.

$$(1)\ Fe \rightarrow Fe^{++} + 2e. \qquad (2)\ CaSO_4 + 8H^+ + 8e \rightarrow CaS + 4H_2O$$

These are followed by hydrolysis of the sulphide and reaction with the anodic products.

$$CaS + 2H_2O \rightarrow H_2S + Ca(OH)_2; \quad H_2S + Fe(OH)_2 \rightarrow FeS + 2H_2O$$

giving the complete process of corrosion as

$$4Fe + CaSO_4 + 4H_2O \rightarrow FeS + 3Fe(OH)_2 + Ca(OH)_2$$

That this is the normal course of the reaction is shown by the constant ratio (1 to 3) of FeS to $Fe(OH)_2$ found in the products of corrosion.[9] Several strains of bacteria, under the general title of *V. Desulphuricans*, are active in the cathodic reaction. They can only flourish when a trace of hydrogen is present, but this will always be supplied by iron and water reacting in air-free conditions. There is in all soils a plentiful supply of these organisms, and they are curiously resistant to a number of ordinary antiseptic agents. Selenium and tellurium complexes have been the most successful inhibitors, but these are relatively expensive. Work on the inhibition of this action is being actively pursued in various centres,[10, 22] but at present it is necessary to lay pipes in concrete or gravel if this very rapid and destructive form of attack is to be avoided. The sulphide-hydroxide deposits do not appear to protect the pipe in any way, while bacterial infection of the surrounding soil increases rapidly as corrosion proceeds. The metal of a substantial cast-iron pipe can be almost completely removed, leaving the graphite flakes still in position. For this reason the attack is sometimes referred to as "graphitisation". Of course, the graphite flakes have little or no strength, and the pipe will either burst under internal pressure, if carrying water, or develop large and ungovernable leaks when carrying gas. If a concrete covering is used, as suggested above, it should be complete, or cracks may act as a centre for intensive local corrosion. It is customary to cover pipe-line sections with bitumen or coal-tar pitch, combined with hessian wrappings to give more elasticity. Such protection as this can give is often confined to the first five years, when the hessian, attacked by other forms of bacteria, rots and disintegrates the bitumen.[11] If the protection is to be effective for twenty years or more, it is better to rely on a heavy coating of bitumen - up to half an inch in total thickness. Glass cloth is now being introduced instead of hessian. Other possible forms of pipe protection are dealt with in a later chapter.

A very common type of local corrosion in chemical works or industrial neighbourhoods generally is caused by "stray" electric currents. Any current-carrying earth wire, such as a tramline, will give rise to stray currents in the neighbourhood passing from soil to buried pipe and back again to soil at suitable electrode points, with corresponding electro-chemical action. It is also common practice to earth small electrical equipment by connecting to the nearest metal pipe that appears to go underground. In one typical case[12] a steel gas main, conveying coal-gas under pressure, was found to be at a steady potential of 230 volts above the surrounding soil. This was due to a mistaken connection, but in another case a steady potential of only 1 volt caused local perforation of a new steel pipe in less than three months. The damage caused by these electrical leakages is often settled by the conductivity of the soil, but where a pipe fails suddenly by localised corrosion, without the blackening which indicates bacterial action, electrical leakage may be suspected. Methods for the measurement of potential differences between pipe and soil have been discussed by Spencer,[13] who recommends a copper/copper sulphate electrode arranged as shown in Fig. III–14. For the full protection of conductor rails, special methods of electrical protection have been devised, for which reference may be made to a paper by de Brouwer.[14]

Corrosion by Specific Chemicals

The sections above have made no discrimination between cast iron and other forms of the metal. When dealing with specific chemicals, it is necessary to make some distinction between iron castings and mild steel or, on occasion, wrought iron. The rate of attack of all dilute aqueous solutions on cast iron depends in the first place on the acidity of the solution. Fig. III-15 suggests the way in which corrosion rates vary with acidity and with oxygen concentration. These measurements have been made at atmospheric temperature, and show that the attack becomes ungovernably rapid at a *p*H of below 3. Total amounts of corrosion will be determined in any

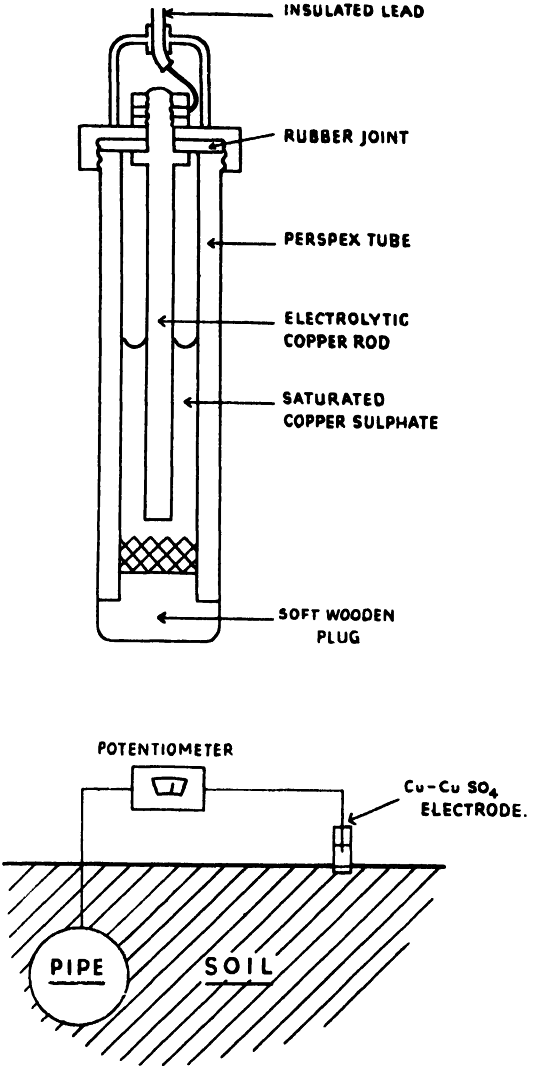

INSULATED LEAD
RUBBER JOINT
PERSPEX TUBE
ELECTROLYTIC COPPER ROD
SATURATED COPPER SULPHATE
SOFT WOODEN PLUG
POTENTIOMETER
Cu-Cu SO4 ELECTRODE.
PIPE
SOIL

FIG. III-14.—Cu-CuSO$_4$ ELECTRODE FOR SOIL CORROSION TESTS.
(After Spencer, *Iron & Steel Inst. Symposium*, Dec. 1951)

specific case by the rate of removal of reaction products, but all dilute acids will attack cast iron far too rapidly for commercial usage. On the other hand, attack is negligible with any definitely alkaline solution, and unless the solution is strongly aerated effects become very small at any pH greater than 8.

The iron is converted to more or less soluble ferrous or ferric compounds when attacked by acids, while a network of graphite flakes often tends to increase corrosion rates by providing intimate cathodic areas. If this is absent, as in the austenitic nickel alloys, or in a chilled "white" cast iron, rates of attack are very substantially reduced. There is still a quite considerable variation in the surface even of these special cast irons, and no passive state due to a perfectly uniform surface can be obtained. It may be possible to reduce rates of corrosion in dilute acids, but that is all.

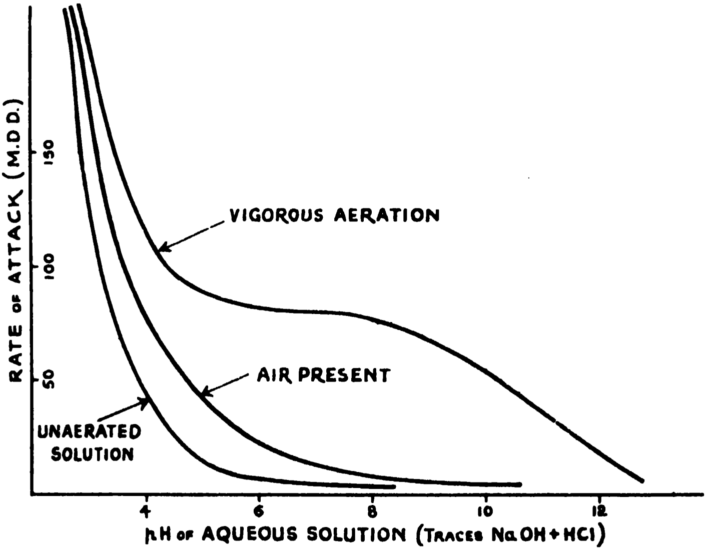


FIG. III-15.—CORROSION OF CAST IRON.

The action of salts in solution will be determined in the first place by the degree of acidity developed, and secondly by the tendency of the ions present to break up or form protective skins over active areas. The action of hard waters containing $CaHCO_3$ in forming a deposit of $CaCO_3$ at basic cathodic areas has already been mentioned, while the opposite action of sodium chloride in providing soluble electrode products is very marked. Even in the latter case total attack is determined by the amount of oxygen available to depolarise the cathodic areas, and will be negligible in the absence of air or other oxidising agents. This is frequently the case with closed chemical plant, where cast iron can be freely used for dilute salt solutions with a *p*H on the alkaline side of neutrality. It is possible for the acidity to increase to a *p*H of 5 when air is definitely excluded, but aerated solutions of this hydrogen ion activity can cause serious corrosion. Sea water, a complicated mixture of almost every metallic salt, with a tendency to deposit magnesium and calcium scales, attacks the metal at rates varying from 20 to 40 mdd, which is rather too fast to be disregarded, even with a cheap constructional material. Nevertheless, cast-iron pipes are commonly used for handling large quantities of sea water, being preferred to steel pipes on account of the greater thickness of metal to withstand pitting.

Oxidising salts in a feebly acid solution can act either as cathodic depolarisers or as anodic inhibitors. Ferric, cupric, and mercuric compounds react in the first manner, giving corrosion rates far above any economic figure. A 4% solution of ferric sulphate, pumped by a cast-iron system, can give rates of attack of the order of 5000 mdd, with considerable pitting. Solutions of nitrates, chromates, nitrites, and permanganates all form protective anodic films, which may be potent enough to check the attack of feebly acid solutions containing such penetrative ions as chlorides. This inhibiting action will be discussed in more detail when dealing with mild steel. Unless some such inhibitor as the above is present, all salts giving an acid reaction in solution will promote attack on cast iron. Ammonium salts are particularly active, corrosion increasing with concentration despite the lower solubility of oxygen and corrosion products. The attack is almost completely inhibited in the presence of free ammonia, and cast iron is widely used in the handling of gasworks liquor. This solution contains free and combined ammonia, with a wide range of acid ions including chloride and sulphide.

The destructive action of dilute acids has been mentioned, and the table on page 72 sets out typical figures for corrosion rates, with some indication of the effect of aeration. The numbers refer to loss of weight in milligrams/sq. dm./day.

If the maximum economic rate of attack is set at 100 mdd, or 0·02 in. of thickness per year, then ordinary cast iron cannot be used for any of the commoner dilute acids. Addition of inhibitors

TABLE III-2

Acid		Rate of attack	
		Oxygen-saturated	Hydrogen-saturated
Sulphuric Acid	6%	2100	180
	50%	1500	1100
Hydrochloric Acid	4%	2800	180
Nitric Acid	1·2%	11,000	9000
	10%	58,000 (aerated)	
Acetic Acid	6%	3200	37
Butyric Acid	1%	142 (aerated)	
Lactic Acid	1%	144 ,,	
Citric Acid	0·2%	110 ,,	

may check reaction for a time, but the practice cannot be recommended for ordinary plant conditions.

Sulphuric Acid

The action of sulphuric acid solutions on cast iron is of major industrial importance. In Fig. III–16 the rate of attack is plotted against H_2SO_4 concentration from 50% up to the anhydrous acid and beyond into the "oleum" range—solutions of SO_3 in anhydrous acid. The rate of weight loss appears to pass through a minimum at about 75% of acid, and fall again after reaching a new maximum

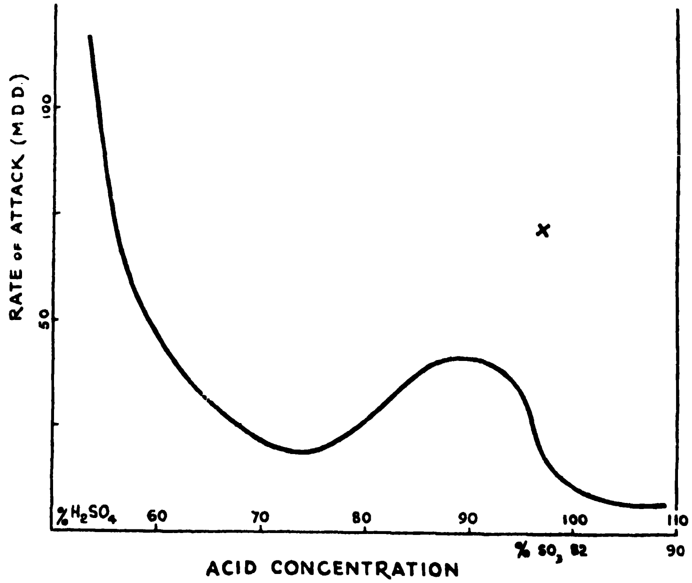


FIG. III–16.—ACTION OF COLD H_2SO_4 ON CAST IRON.

at 90%. This increase between 75% and 90% is not serious, and for all strengths of acid above 65% cast iron is a possible material of construction. The figures for oleum are somewhat doubtful, and an isolated measurement of 70 mdd suggests that localised corrosion can sometimes occur. This takes the form of cracks, perhaps following the grain structure, but ultimately causing breakage in cast-iron pipes. As a result, oleum coolers for SO_3-absorption units are now made up in cast steel, though many cast-iron sections are still in use. The corrosion rates quoted have been for cold acid, but increases in temperature do not seem to cause a rapid increase in attack. Cast-iron pipe-lines conveying oleum at 50°–60° C. are not corroded away, though they may crack, and a working life of five to ten years is obtained. Enamelled cast-iron pipes are sometimes used for this duty, and have the possible advantage that attack through micro-cracks in the enamel is not serious.

The resistance of iron in all its normal forms to the attack of concentrated sulphuric acid is due to the formation of an insoluble sulphate skin over the entire metal surface. This must be largely active as an anodic inhibitor, for the acid could liberate hydrogen or be reduced to SO_2 at cathodic areas with ease. Breaks in the surface caused by erosion or cracking will cause local corrosion in the usual way, but the acid can and does repair such breaks. If erosion is severe, then the iron can be corroded through a considerable thickness of metal in a few months, a point brought out below in discussing pot concentrators for sulphuric acid. When the coating is undisturbed, corrosion grows steadily slower with the years, and many cast-iron sections working on 90–96% acid have been in constant use for ten to twenty years. Attack in such cases is commonly due to spillage, followed by dilution with moisture from the air, or by emptying of the plant, when moist air again causes dilution to active concentrations. If plant is filled or emptied frequently, it may be worth-while to fit a breathing device on the air inlet, filled with a drying agent such as silica gel or activated alumina.

Manufacturing processes demand that large quantities of SO_2 be handled in contact with more or less concentrated acid. As long as the water content of the solutions does not increase much above 30%, the presence of SO_2 does not increase attack, except perhaps at moving parts such as valves or pumps. All valves on acid plant are liable to stick, and this trouble is particularly marked with the mixture above. Stoneware taps have been recommended [15] to prevent such trouble, but if these stick they are easily broken, and a well-lubricated cast-iron plug cock gives very little trouble if properly maintained. Large towers for gas treatment are made up in steel because cast-iron sections would be very unwieldy, but the pipe sections are commonly of cast iron—provided, as before, that the acid concentration does not drop below 70% H_2SO_4 or thereby. For the more dilute acids lead-lined pipes are normally used, as indicated in the appropriate section. Centrifugal pumps for concentrated acid are usually made with a cast-iron shell and a cast-iron or silicon-iron rotor mounted on a mild-steel shaft. The complex forms of a centrifugal pump can readily be made by casting, and pumps of an ordinary type are so cheap that a relatively high rate of corrosion can be accepted. It is good practice to mount two pumps side by side in parallel, so that one can be replaced while the other is on load. Many contact sulphuric acid plants work on sulphur, which is melted and pumped to the burner through a cast-iron centrifugal pump. As long as the sulphur is dry, it will have no apparent action on the metal unless the temperature exceeds 250° C., a most unlikely contingency. Aeration and moisture increase the rate of attack, even at atmospheric temperatures, to quite unworkable proportions. Mixtures of sulphur, water, and air can destroy a cast iron pump completely in about three months. Traces of ammonium bicarbonate (0·5 lb./ton of sulphur) have been used for neutralising the effects of a slightly damp sulphur, but if the water content rises above 5%, there is little to be done.

One of the great advantages of the contact process for sulphuric acid is that no appreciable amount of acid below 70% H_2SO_4 need be handled, and this means that it is sometimes possible to build the plant entirely in cast iron or steel. In the chamber process, a final acid strength of 70–75% means that very little iron can be used. The acid can, however, be concentrated in large cast-iron pots set in brickwork and heated by direct firing. These pots, as shown in Fig. III–11, are about 7 ft. in diameter by 7 ft. deep, and when in use are filled with boiling sulphuric acid of 95–97% strength. Attack is fairly rapid in a new pot, but soon decreases, and the working life is from five to seven years. Failure is usually caused by cracking in a position suggesting thermal stress, though probably this is accentuated by corrosion. It is possible to obtain a heat flow of 6000–7000 B.Th.U./sq. ft./hr. through a cast-iron wall of about 2 in. in thickness. According to Parrish,[16] the cast iron for such plant should be as low in nickel as possible, with a high silicon content. Casting should be done with the flange side of the mould uppermost, and with a good liquid head over the flange to collect slag inclusions. The cast flanges should carry slots for bolts rather than be drilled after casting, and particular care taken to avoid sudden changes of section. It has been suggested that a groove should be cut at the acid surface line, and this groove filled with acid-resisting brick, so that chance dilution when the plant is shut down, or surface agitation, shall be better resisted. The complication is hardly worth the extra cost involved. In many of these pots a stirrer was fitted to improve the ordinary thermal agitation and to prevent the settling of sludges, but it was found that the erosion caused by these very sludges, forced round by the stirrer, set up such corrosive effects that the pots failed very rapidly.

The highly successful use of cast iron for concentration pots is a sufficient indication of the resistance to boiling concentrated acid, but if the water content ever rises above about 15%, the metal is rapidly attacked, due no doubt to solution of the protecting ferrous sulphate. More dilute acids will also be extremely corrosive at boiling-point, and it is generally undesirable to use cast iron in contact with any hot sulphuric acid solutions if the water content is more than about 10%.

Nitric Acid

Nitric acid, *alone*, attacks cast iron rapidly at all strengths, even when cold. Passivation of iron by strong nitric acid is too uncertain for any reliance to be placed on its effect, and in any case the action is more marked with steel than with cast iron. Thus cast iron in 94% HNO_3 can lose weight at a rate of 6000 mdd, while mild steel has been claimed to lose only 40 mdd in similar circumstances. It is always possible for the protecting film to break down, and neither cast iron nor steel can be safely used for nitric acid of any strength. Nevertheless, if some 10% of concentrated (96%) sulphuric acid is added to concentrated nitric acid of above 60% HNO_3 it is possible to store the mixture in steel tanks and to pump with cast-iron pumps. The two acids have, in fact, a notably modifying effect on each other—a very useful property when dealing with nitrating acids. These mixtures of sulphuric and nitric acids are almost inert to cast iron at all temperatures up to 110° C., provided that the amount of water present in the mixture does not exceed about 35%. Cast-iron nitrators, working at temperatures from atmospheric to 110° C., have been used almost continually for more than five years with little or no corrosion. Similarly, nitrating acids can be pumped by cast-iron centrifugal pumps, though a cast-iron shell and a silicon-iron impeller give a better long-term performance.

Hydrochloric Acid

Hydrochloric acid attacks cast iron rapidly. A general rule can be laid down here. *Hydrochloric acid, in any concentration, attacks iron in any form too rapidly for commercial use.* The *dry* HCl gas has no action at temperatures below about 150°–200° C., but above this level will tend to form volatile chlorides by direct combination. Solutions of the other halogen acids are almost equally active in the corrosion of cast iron, with the exception of hydrofluoric acid. Aqueous solutions of this acid should not, in general, be handled in cast iron, but if the acid solution is cold, and contains more than 60% of HF, attack will be slight.

Phosphoric Acid

Phosphoric acid in all strengths will attack cast iron at uneconomic rates, especially if pure. A crude acid, made from phosphate rock by the "wet" process of reaction with sulphuric acid, contains traces of calcium sulphates and fluorides. These tend to give an inhibiting skin, while the phosphoric acid itself can act as a passivating agent. Short exposure of iron surfaces to the action of phosphoric acid, combined with proprietary inhibitors, gives a skin which is resistant to atmospheric or aqueous corrosion. The process, known under various trade names (Parkerising, Bonderising, Jenolising, etc.), is more important when applied to mild steel, when a very suitable surface for paint application is obtained. Continued exposure to the acid solution will pit both cast iron and steel badly.

Organic Acids

Aqueous organic acids, as shown above, all attack cast iron, but if insoluble iron salts are formed the corrosive effects may not be very serious. The benzoates in solution have been shown to act as inhibitors of iron corrosion, and their action in acid conditions could probably be compared with phosphoric ions. Owing to the cheapness of cast iron, it will always be used when corrosion is moderate and iron contamination unimportant. This situation frequently arises in the distillation and refining of coal tar, petroleum oils and similar "natural" products. Here a wide range of feebly corrosive agents are in solution in an inert medium. Unless conditions are unusually severe, as in high-temperature distillation or the processing of almost pure phenols, cast iron is quite suitable for all organic liquids. Corrosion troubles are usually initiated by the presence of water, which provides a dilute acid solution, though organic sulphur compounds may decompose to give corrosive gases. A cast-iron distillation column, with austenitic nickel alloy bubble caps, has given quite satisfactory service in the distillation of crude tar acids. Pumps for hot coal tar are made with cast-iron bodies, though monel-metal fittings and valves (for a reciprocating pump) are usually employed. It is often possible to check corrosion in petroleum stills by the injection of small amounts of ammonia.[23]

Alkalies

Aqueous solutions containing free alkali will not attack cast iron in any way until high concentrations and temperatures are reached. For caustic soda and the like, the corrosion rate is negligible, even at boiling-point, until a free NaOH concentration of about 30% is reached. Above this level the action of alkali is to form a soluble ferrite and to liberate hydrogen, with solution rates that may rise to over 1000 mdd as the NaOH concentration passes 50% by weight. These rates are measured by immersion of cast-iron specimens in a caustic solution, and do not detect the more insidious attack which may take place as "caustic embrittlement". This phenomenon has been widely studied in connection with mild steel and is probably a typical case of stress corrosion. As such, it is not likely to be so important with cast-iron plant, which is seldom under a marked mechanical stress. None the less, it is obviously desirable to avoid strongly alkaline conditions with an ordinary cast iron, even if there is no likelihood of stressed conditions. The nickel bearing alloys are more resistant, perhaps because fewer grain boundaries are presented in an austenitic metal. Despite these drawbacks, a typical caustic soda fusion pot, for final stages of solid caustic manufacture or for many organic reactions, is made from cast iron. A mixture of NaOH and sodium metal can attack rapidly.[25]

HIGH-TEMPERATURE RESISTANCE

As mentioned above, all cast irons begin to lose strength at 400°, and the loss is rapid above 500° C., which represents a practical working limit. Nevertheless, the metal is so cheap that a very heavy section can be built to take slight loads at slightly higher temperatures. Many good casting alloys containing silicon, chromium, or nickel have been developed for such conditions, and the use of an ordinary cast iron is not recommended.

As might be expected, the rate of oxidation in air goes up steadily with temperature, and becomes very rapid above 750°, as shown in Fig. III-17. The measurement, it will be noted, is by gain in weight, and represents adherent scale. Following the laws of direct attack, as laid down in Chapter I, it would be expected that an oxide film will slow down rates of attack to some extent, but this is not very obvious in the case of iron, especially when the temperature exceeds about 200°. The oxide layers have been found to contain all three of the characteristic iron compounds FeO, Fe_3O_4, and Fe_2O_3, with the latter in the outer layer. As the temperature of oxidation falls, the ferrous oxide disappears, leaving only magnetic iron oxide and the fully oxidised Fe_2O_3.[17] Perhaps at ordinary temperatures in dry air, the very thin films of oxide would consist of Fe_2O_3 resting directly on the surface. Clearly the mechanism of oxidation consists in reaction of oxygen at the oxide surface with a stream of iron atoms which pass at steadily increasing velocity as the temperature increases, causing a form of reduction wave to exist in the film. This is accompanied by considerable volume changes and a consequent porosity, so that the film can easily transmit reactants and gives no real protection. The more complete film formed at low temperatures is actually more difficult to remove than the thicker scales formed at 600° and upwards.

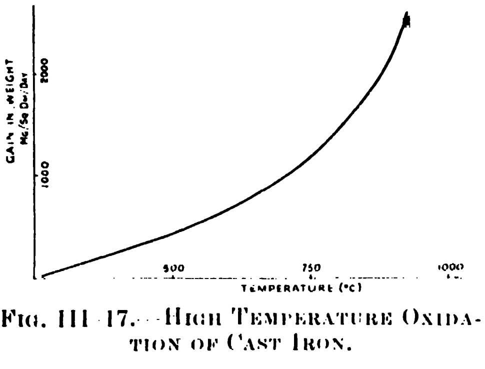


FIG. III-17.—HIGH TEMPERATURE OXIDATION OF CAST IRON.

Apart from this general surface oxidation, cast iron is subject to a particular form of attack known as "growth". When heated and cooled alternately to temperatures above 500° all normal cast irons tend to increase in volume. As the temperature increases into the region in which conversion to an austenitic form can occur, this growth becomes more marked. Oxidising conditions increase the growth—in fact some form of oxidation may be essential. The causes of this phenomenon have been widely discussed,[18] but it seems probable that some form of "respiration" or alternate sucking in and discharge of gases is the primary factor. This action can be accentuated by the alternate passage of carbon into and out of solution, as in the formation of austenite or its decomposition, while the slow decomposition of cementite to form graphite may produce easily oxidised phases. Such decomposition alone can produce a considerable expansion, but growth in both white and grey cast irons appears to continue after this change. Nickel and silicon in small quantities increase the tendency towards growth, although in amounts exceeding 5% both these elements can produce special heat-resistant alloys. At temperatures around 1000° C., the carbon in the iron is oxidised, and the space so formed is filled with iron oxide, which has been supposed[19] to force the grains apart and expose fresh surfaces for attack. Other gases than oxygen (in particular steam and the oxides of carbon) are active in causing growth. Hot producer-gas at 700° can give a very rapid growth, ½-in. bars of metal increasing to double this thickness in about six months. The section of these swollen bars was curious, seeming to be made up with a carbon centre and an outer layer of iron. This may be an example of catalytic action, as in the oxidation of H_2S over iron oxide, when a sulphur core is formed inside an iron oxide skin.

Whatever the mechanism, this growth phenomenon forbids the use of cast iron at temperatures in excess of 500° C., even in reducing conditions. Of course, when active corrosive agents such as chlorine or the other halogens are present the temperature must be lower—perhaps not above 200° C.—while sulphur dioxide attack becomes uneconomically rapid at about 400°.

MALLEABLE CAST IRON

This form of metal has been developed in an attempt to confer on a relatively cheap casting the essential properties of a mild steel. Manufacture consists in preparing a normal casting, with little silicon or phosphorus, so that the primary form is a white cast iron of even quality. This casting, or a number of small castings, are packed into closed iron "cans" of a heat-resisting alloy and heated in a furnace to a temperature of about 900°. The heat is maintained for three to four days, during which time the cementite gradually decomposes to graphite and ferrite, while the pearlite reassumes an austenitic form. Subsequent cooling is slow, and more graphite is deposited rather than cementite, so that the final form is largely one of ferrite and graphite, the latter in fine flakes or even nodules. Owing to the mode of cooling, the interior of the casting has the highest content of free carbon, and in consequence is known as "blackheart malleable iron". A corresponding "whiteheart malleable iron" can be obtained by packing the castings into position, before annealing, with an oxidised mill scale mixtures of Fe_2O_3 and Fe_3O_4. The ferric oxide reacts with carbon to give carbon dioxide and lower oxides of iron, while the residual ferrite can finally be freed almost entirely from all graphite or cementite. Both these irons, and particularly the latter, correspond to a true wrought iron in physical structure, except that the laminar slag inclusions (see Chapter IV) are absent. A third but somewhat less common form of malleable iron has been made by cooling the castings rather more rapidly after the austenitic form has been established, and obtaining a pearlitic structure.

Malleable irons are chiefly valued for toughness and machineability, finding their most common use in pipe joints and valve fittings. The cost of making a simple pipe union in mild steel, turning up all parts from a solid bar, is very much higher than the casting of special sections in a multiple mould, followed by annealing and machining done on an almost ideal material. A possible drawback is the surface softness, and a blackheart iron can be rehardened by heating and quenching, though this is hardly ever done.

Specific corrosion tests on malleable cast irons are rare, but the essential physical structure suggests that they will behave in the same way as good cast iron, with the whiteheart, as more homogeneous, giving the better results. In Fig. III–18 the carbon forms are very reminiscent of "nodular" high-duty cast iron, as shown in Fig. III–9, and a pipe fitting made from this material would combine well with pipes of the nodular iron in resisting strong sulphuric acid.

The mechanical properties of malleable irons are covered in British Standards,[20] which call for an ultimate tensile strength of the order of 20 tons/sq. in. and a satisfactory bending test.

Alternatively to this last, the phosphorus content is limited to below 0·1% for whiteheart and 0·2% for blackheart.

LOW-ALLOY CAST IRONS

With such a popular material of construction as cast iron, it is obvious that over many years almost every known element has been incorporated in the hope of obtaining better mechanical properties or some ease in working. All normal castings contain inclusions of this kind, as mentioned above, while a special chapter (Chapter V) is devoted to the numerous ferrous alloys, many of which could logically be included under this heading. A few special modifications in cast iron can, however, be included here.

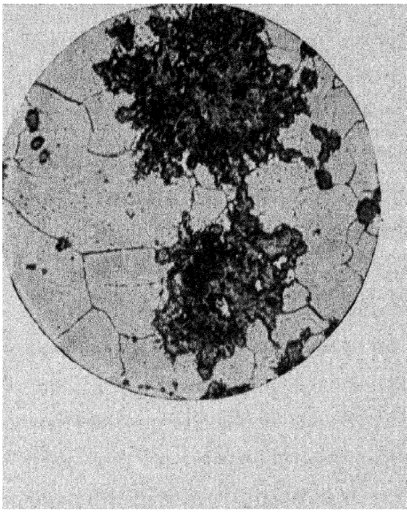


Fig. III-18*a*.—Blackheart Malleable Cast Iron.

(From Woodward, "Engineering Metallurgy")

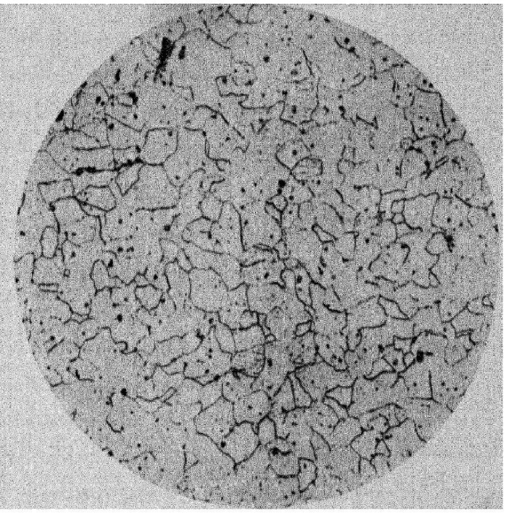


Fig. III-18*b*.—Whiteheart Malleable Cast Iron.

(From "Metallurgical Materials". *Courtesy of V. N. Wood, Esq., and Messrs. Chapman & Hall, Ltd.*)

The first of these are the temperature-resistant alloys containing silicon. If this element is present in amounts up to perhaps 4%, the tendency is for growth to be more marked, as mentioned above (page 79), but when the silicon is increased in amount to 6% and more, the effect is in the opposite direction. The Silal[21] group of heat-resisting cast irons, with 5–10% of silicon, can be used safely up to 850° without any serious attack by air. These alloys form essentially a silico-ferrite matrix and finely divided graphite. In the presence of silicon the temperature at which ferrite forms change to austenitic iron is raised to above 900°, and this may be the principal factor in protection. As long as the silicon content does not exceed 10%, the irons can be machined, as distinct from the special acid-resisting silicon iron (Chapter X). They have, however, no particular advantage over ordinary cast iron from the point of view of corrosion resistance. The presence of silicon makes the ferritic base somewhat brittle, and this can only be overcome by incorporating sufficient nickel to stabilise an austenitic structure. The "Nicrosilal" so formed, with 18% of nickel, can hardly be described as a low-alloy cast iron.

Wear resistance is not normally of great importance on chemical plant, but where this is required it is necessary to decrease the amount of ferrite present, either by chilling or altering the composition to give increased amounts of the harder carbide compounds. The brittleness of the finished iron is an obvious disadvantage, and this can be partially overcome by stabilising the austenitic form and heat treating to give martensite. The most obvious addition is nickel, which in amounts of 4–5% will give a martensitic form to the ordinary casting. The "Ni-hard" group of irons contain about 5% of nickel, with some 1% of chromium and a low silicon content. By varying the carbon content from 2·5 up to 3·5% a gradual increase in hardness (from 550 to 650 Brinell) is obtained at the cost of some embrittlement. Manganese and molybdenum will always increase the hardness of a casting but are somewhat costly additions. Special cast irons containing these additions alone are therefore unusual, and would appear to have no great advantage over the Ni-hard irons mentioned above. By suitable adjustment of nickel content (4%), and the addition of both manganese and molybdenum (1% of each), a casting alloy can be obtained which gives the so-called "acicular" iron. This is a form of iron structure intermediate between pearlite and martensite, having tensile strengths of 25–35 tons/sq. in., and an impact resistance (Izod test) as high as 45 ft.lb. The Brinell hardness is only 300–350, so that castings can be machined, as distinct from Ni-hard, where the martensitic structure gives a figure of 600 or more. On the other hand, acicular cast irons are claimed to be considerably more wear-resistant than an ordinary pearlitic iron, where the Brinell hardness may fall below 200.

As a rule these low-alloy cast irons will not stand up to chemical corrosion any better than a good-quality white cast iron of normal composition. The increased cost of such mixtures will not be justified from a corrosion standpoint, but only from the angle of increased heat resistance or of wear resistance coupled with toughness. For real resistance to corrosion it is necessary to incorporate larger amounts of alloying metal, as will be shown in Chapter V.

REFERENCES

1. Pearce, J. G., *Proc. Chem. Eng. Grp.* (*S.C.I.*), 1948, **30**, 18.
2. See also B.S. 321 and 786.
3. B.S. 1349 (1947).

3*a*. Bewsher, J. N., *Ind. Chem.*, 1949, **25**, 219 and 262.

4. See, e.g., *Chem. Process Eng.*, 1952, **33**, 325.
5. Mears, R. B., and Evans, U. R., *Trans. Farad. Soc.*, 1935, **31**, 530.
6. Vernon, W. H. J., *Trans. Inst. Chem. Eng.*, 1937, **17**, 171.
7. Evans, U. R., "Metallic Corrosion, etc.", *loc. cit.*, p. 185 *et seq.*; also Hudson, J. C., and Stanners, J. F., *J. Appl. Chem.*, 1953, **3**, 86.
8. Hudson, J. C., "Corrosion of Iron and Steel", Chapman and Hall, 1940, pp. 87, 91; also *J. Iron Steel Inst.*, 1948, **160**, 276.
9. Butlin, K. R., and Vernon, W. H., *Proc. Chem. Eng. Grp.*, 1949, **31**, 65.
10. "Chemistry Research", H.M.S.O., 1946 50.
11. Butlin, K. R., Vernon, W. H. J., and Whiskin, L. C., Rept. 45, *Iron Steel Inst.*, 1951.
12. *Trans. Inst. Gas Eng.*, 1950, Communication 374.
13. Spencer, K. A., Rept. 45, *Iron Steel. Inst.*, 1951.
14. de Brouwer, R., *ibid.*, 1951; also Pritula, V. A., "Cathodic Protection", H.M.S.O., 1953.
15. B.I.O.S. Reports, No. 1641, 1642.
16. Parrish, P., *Trans. Inst. Chem. Eng.*, 1941, **19**, 1.
17. Pfeil, L. B., *J. Iron Steel Inst.*, 1929, **119**, 501; 1931, **123**, 237.
18. See, e.g., Evans, U. R., "Metallic Corrosion, etc.", *loc. cit.*, p. 122 *et seq.*
19. Thyssen, M. H., *J. Iron Steel Inst.*, 1934, **130**, 153.
20. B.S. 309 and 310 (1947).
21. British Cast Iron Research Association (B.P. 323076).
22. Farrer, T. W., Biek, L., and Wormwell, F., *J. Appl. Chem.*, 1953, **3**, 80.
23. Chir, V. J., *Inst. Pet. Rev.*, 1953, **7**, 159.
24. Wormwell, F., Nurse, T. J., and Ison, H. C. R., *J. Appl. Chem.*, 1953, **3**, 275.
25. Wallace, T., *Chem. and Ind.*, 1953, 876.

CHAPTER IV

STEEL

As specified in the previous chapter, all alloys of iron and carbon containing less than 1·7% of carbon are known as steels. Referring to Fig. IV–1, it is clear that all mixtures of iron with carbon corresponding to this specification will originally solidify to an austenitic γ form, unless large quantities of other constituents are present or the carbon content is very low. In this latter case, austenitic iron forms rapidly on further cooling. As cooling continues, the lower limits of the γ loop are reached, and either ferrite or cementite is rejected from the austenitic phase. Steels containing more than 0·89%* of carbon will form cementite and those with less will form ferrite. Both will therefore tend towards the eutectoid composition and ultimately the residual austenite will convert to pearlite.

The cooling of a solid steel and the consequent changes have been very intensively studied and certain notable changes should be mentioned briefly at this point. When a curve is drawn for cooling rates from temperatures above 900°, a break is noted when the austenite begins to reject ferrite or cementite. This break is known as the A_3 point for steel, and can be reached either by steady cooling or steady heating--the latter signalising complete conversion to austenite. As there is always a lag in thermal changes of this kind, the A_3 point will be reached at a somewhat higher temperature on heating than on cooling. To differentiate between the two values, heating points are marked by the suffix "c" (from the French "chauffage") and cooling points by "r" ("refroidissement"). Then the Ac_3 point will be reached at a temperature about 20°–30° above that of the Ar_3 point. The next break in heating or cooling comes when the steel loses or gains magnetic properties—Ar_2 or Ac_2. Finally there is a break when the pearlite structure is formed—Ar_1—or disappears—Ac_1. The change in magnetic property is almost constant at 768° for all α iron—ferrite—and this may in many circumstances be above the level at which ferrite first appears

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* Variously reported as 0·85–0·89%.

All these changes need a certain time to effect, and as a result may be more or less effectively delayed by rapid cooling, or definitely completed by suitable annealing. The science of steel-making consists in the careful control of heat treatment, so as to provide a physical structure in accordance with the special properties required. Cementite is very hard, as compared to a ferrite structure. Pearlite, which is essentially an even arrangement of the ferrite and cementite grains (Fig. IV–2), shows a reasonable combination of tensile strength, hardness, and ductility (as measured by elongation under load). The curves of Fig. IV–3, illustrating this point, refer to a very slowly cooled or fully annealed steel. Such a steel is easily machined (Brinell hardness about 200) but is rather too soft for severe abrasive wear and insufficiently ductile for easy rolling to plates or girders. Hardness can be achieved by heating to beyond the Ac_3 point, at which the steel is converted to an austenitic form, and then cooling rapidly past the Ar points. By such "quenching" the austenite is converted to a series of special steel structures in which the crystal form is more or less needle-like, but finally quite homogeneous, with no carbon or carbide separation. Martensite,

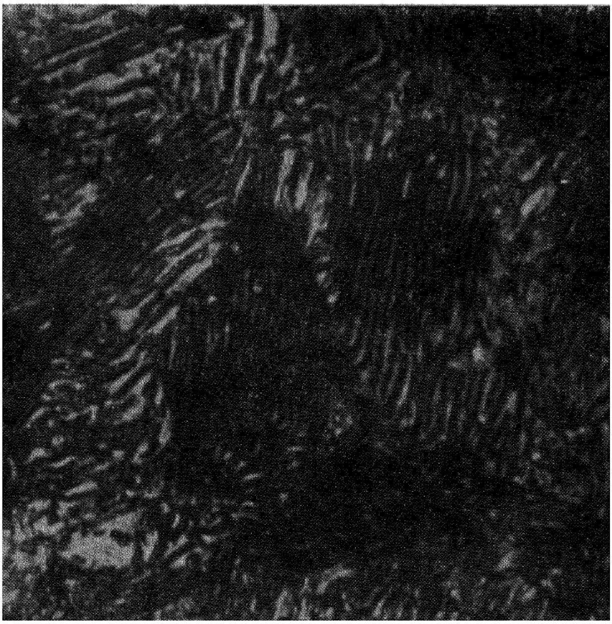


Fig. IV–2.—Lamellar Pearlite.

(Courtesy of Dr. J. M. McLeod, Metallurgy Dept., Royal Technical College, Glasgow)

the hardest of these steels, shown in Fig. IV-4, has a Brinell hardness of about 700, and is formed by controlled quenching. If this quenching is carried to below about 100°, transformation of the austenite to a martensitic form becomes very slow, and a certain proportion of "retained austenite" is found in the finished steel.

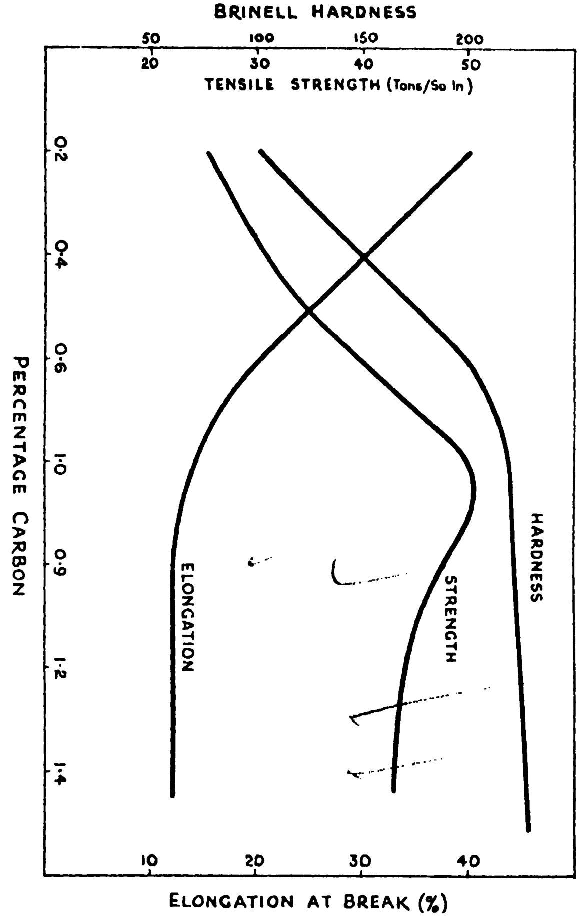


FIG. IV-3.—CHARACTERISTICS OF CARBON STEELS.

This is uncommon in ordinary steels, but may deliberately be sought with certain alloys. The ideal treatment for production of martensite appears to be rapid cooling to about 240°, but trace elements can alter the hardening temperature quite markedly. By intermediate quenching conditions a range of steel forms (bainite, troostite, sorbite) can be formed, with physical structure and properties somewhere between pearlite and martensite.

These hardened steels cannot be formed easily from an austenite with less than 0·2% of carbon, as the ferrite separates prematurely. It will also be appreciated that such heat treatment cannot be applied to large steel sections. The normal structural steel, as used for plates and rolled sections, will contain 0·13–0·35% of carbon. As a mixture of ferrite and pearlite, it cannot be greatly hardened by quenching, though various forms of surface treatment are used. A steel for quench-hardening, which may be confined to the surface, will contain 0·4–0·6% C, while the higher-carbon steels are only used where great hardness is essential, as in saws or cutting tools.

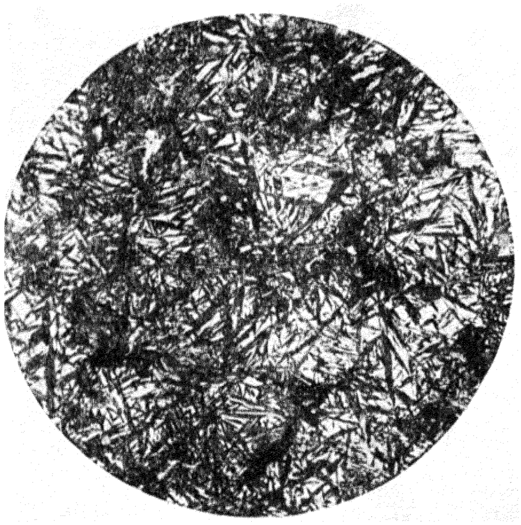


FIG. IV–4.—MARTENSITIC STRUCTURE.
(Courtesy of V. N. Wood and Messrs Chapman & Hall Ltd.)

A fully hardened steel will be in a state of internal stress, and although there are no marked differences in structure, it might well fail by cracking or some form of stress corrosion. Some sacrifice of hardness by "tempering" or reheating to a suitable temperature range will remove this tendency. Such thermal treatment is, of course, of major importance in all forms of special engineering steels, but not generally considered in the steel used for ordinary chemical plant. The tempering varies the properties of a steel to such a wide extent that no general figures can be quoted for these qualities. Considering Table IV–1, which covers the changes made in an ordinary steel of about 0·4–0·45%, it will be seen that a variation in most properties of the order of 50% can easily be made by an appropriate heat treatment.

TABLE IV-1

Condition	Ultimate Tensile Strength	Elongation at break	Brinell Hardness
	Tons/Sq. In.	Per Cent.	
Fully hardened	68	1·5	360
Tempered at 200°	65	4	330
Tempered at 300°	62	9	270
Tempered at 400°	57	15	250
Tempered at 500°	49	19	220
Tempered at 600°	43	25	200
Tempered at 700°	38	31	185

A further effect of quenching to a martensitic form is the elimination of the sharp yield-point shown by annealed steel. This point is brought out in Fig. IV-5, where the effects of prolonged cold-working— work-hardening—are shown to be similar. At the same time an Izod impact test of 80 ft.lb. is reduced by quenching to 15, while the Vickers hardness increases from 130 to 450. All these changes are for a typical 0·3% carbon steel, and again illustrate the wide range in properties with thermal history of the specimen.

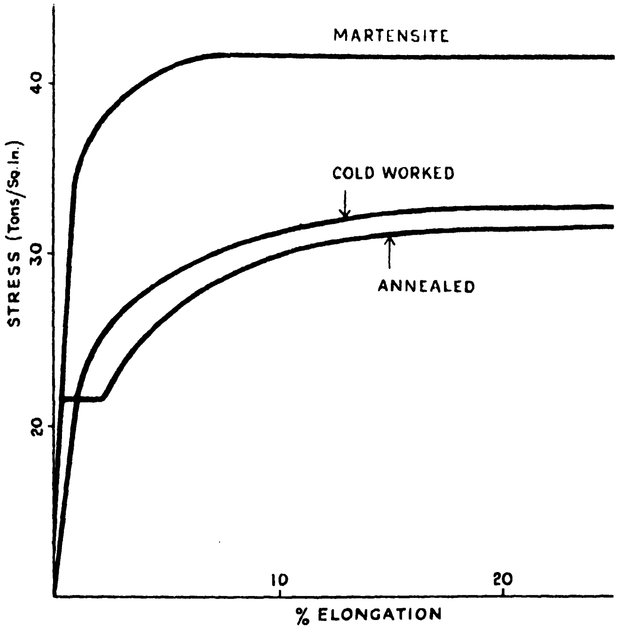


FIG. IV-5.—EFFECTS OF COLD WORKING OR QUENCHING.

The effect of temperature on strength for a similar steel to the often met with in the larger sections of chemical plant. Following the general rule that any factor tending to produce an even surface structure will diminish corrosion, it can be anticipated that a case-hardened steel will be more resistant to chemical attack than before treatment.

So far only carbon has been considered as the property-determining additive to pure iron, but almost every other element has been used as a modifying agent. Manganese is generally added to get rid of sulphur and oxygen, but any excess dissolves in the iron to increase mechanical strength. A steel containing more than 1% of Mn will be tougher, stronger, and harder than normal steel, but is not commonly used for ordinary steel work on the score of expense. Silicon is always present, as with cast irons, but in lower quantities (0·2%). The amount is often increased for steel castings, as in amounts up to 0·5% the grain structure is improved. Lead and sulphur, in about the same amounts as with silicon, have been added to improve machining qualities. The special alloy steels used in chemical plant will be considered in the next chapter, and only normal carbon steels, with no other addition of importance, referred to here.

FABRICATION OF STEEL PLANT

Modern mechanical technology is based almost entirely on the properties of steel. The methods of hot and cold rolling or pressing, of riveting, welding, drilling, and tapping with screw threads, have one and all been evolved with mild-steel fabrication in view. Naturally, therefore, all forms of machine-shop technology can be used with a good steel. Riveting is becoming obsolete, especially for vessels built to withstand both pressure and corrosion. A welded unit can be made up with equal strength and with no crevices or stressed portions to invite chemical attack. The only possible advantage of riveting is that a large vessel can be more easily assembled at the site, but even this is debatable. A welded steel vessel can be built with a smooth interior finish—very important in cases of batch production and intermittent cleaning—and has the same mechanical reliability as riveted work, provided that the welds have been properly inspected. Specifications[1] for a welded steel air receiver call for hydraulic tests to one and a half times the design pressure, with hammering of all welds while under test. The pressure must then be released and reapplied to twice the design pressure for 15 minutes. Other provisions call for specific methods of welding, a minimum thickness of plate, regulation of end design, and means for testing the weld metal.[30] The only constituents limited specifically are sulphur and phosphorus, which must both be below 0·05%, while the steel of the plate must have a minimum ultimate tensile strength of 24 tons/sq. in. Marine boiler steel must have a somewhat greater strength, with an elongation at break of 20–23%, and similar maxima for sulphur and phosphorus. The plates for boiler work must be as free as possible from scale inclusion, a precaution that should be taken generally with chemical plant steel. If a hydrogen-liberating agent is present, the gas can and does diffuse through steel, but it cannot pass a slag inclusion. Then the hydrogen seems to build up an internal pressure sufficient to raise a blister on the metal surface and rapid corrosion can follow.[2]

Reactions calling for high pressures and temperatures are always carried out in steel equipment, although special alloys or liners may be used. Fabrication can be carried out by "forging", or the shaping of a single piece of metal by heating and hammering. Ordinary mild steel is particularly suited to this treatment, and very large vessels of over 100 tons in weight can be made in suitable machine shops. The detailed design of such plant is perhaps the most difficult problem in "classical" engineering met with in chemical plant, where corrosion is usually of much more importance than a careful analysis of stress. A brief outline of pressure-vessel design is set out in the next paragraphs in order that the factors involved may be appreciated.

If a thin-walled cylinder is under internal pressure, it may be assumed as a first approximation that the stresses in the walls due to this pressure are evenly distributed over the entire wall section. Considering the case of a cylinder with length L and diameter D under a pressure p, as shown in Fig. IV–7, the stress S per unit area of material, resisting rupture along the length of the cylinder, is given by

$$2L.S.t = L.D.p$$

where t is the wall thickness. It follows that if S is defined as the maximum working stress for the metal of the wall, then the minimum working thickness t is given as

$$t = D.p/2S$$

This is the so-called "hoop stress" on the cylinder, but there is also a smaller force exerted from the ends and tending to pull the cylinder apart along a circumferential section. Using the same nomenclature

$$\pi . D . S . t = \pi . D^2 . p/4 \text{ and } t = D . p/4S$$

The resistance of a shell to rupture in this way is twice the value for a hoop stress rupture, so that for a uniform cylinder only the latter need be allowed for. A glance at the formula for wall thickness shows the reason why any vessel to withstand internal pressure should be as long and narrow as other design considerations will allow.

If the thickness of the wall given by this formula is more than 10% of the diameter, then the primary approximation is no longer justified. Stress will vary across the wall, and a number of formulae based on mathematical analyses have been proposed. The first and perhaps most popular was due to Lamé, and states that

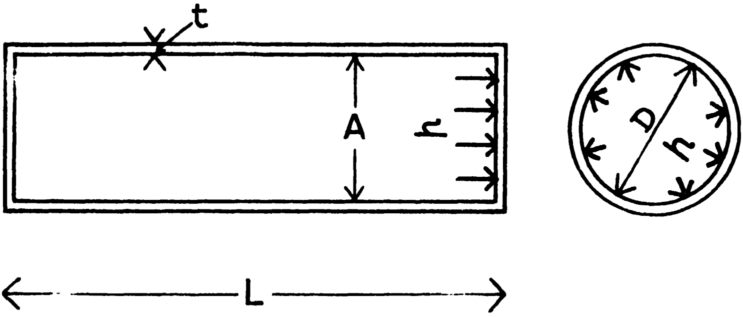


FIG. IV 7. VESSEL UNDER INTERNAL PRESSURE.

$$t = \frac{Di}{2}\left[\sqrt{\left(\frac{S+p}{S-p}\right)} - 1\right]$$

where *Di* is the internal diameter. This is the most easily applied form of Lamé expression, but another general form is

$$\frac{p}{S} = \frac{R^2 - 1}{R^2 + 1},$$

where *R* is the ratio of external to internal diameter. The extension of these expressions to cover the actual breakdown of a cylinder under internal pressure has led to considerable discussion on the manner of mechanical failure, and no very definite decisions have been reached. Any programme of testing will obviously be very expensive, and the simple formulae above, used with a reasonable value for the safe stress, appear to have given satisfaction. For further discussions on this point the reader is referred to the work of Newitt[3] or Comstock.[4] British Specifications have been tentatively laid down in B.S. 1500 (1949).

As many pressure vessels will be used for long periods at temperatures well above normal, the importance of creep-stress determinations becomes obvious. The stress for a standard creep strain of 10^{-6} in. per in. may drop more rapidly with temperature than the elastic limit, which usually represents the maximum safe load. In a typical case for 1% Cr steel, the elastic limit dropped from 30·3 to 29·5 tons/sq. in. as the temperature of test rose from 450° to 500°, but the limiting creep stress dropped from 23·8 to 11·5 tons over the same temperature range. Again a 21% Cr, 7% Ni steel has an ultimate strength (short-time tensile test) of 24·6 tons, but a limiting creep stress of only 1·3 tons—both at 800° C.[5] It is usual to base design on a safe load of $\frac{1}{3}$ to $\frac{1}{2}$ of the elastic limit stress, and this may be a sufficient reduction to meet the normal creep requirement of less than 1% extension over 100,000 working hours.[6] An additional effect of heat will be the development of temperature stress in the metal wall, which may reinforce the normal load if the vessel is heated externally. This is too complicated a subject to be dealt with here, and reference should be made to the work of Newitt cited above.

When the pressure vessel is not forged from one piece of metal, but built up by riveting or welding, some allowance must be made for the efficiency of joints, while a further weight of metal must be allowed for possible corrosion in many cases. As mentioned above, riveting is apparently becoming obsolete, and the typical boiler drum, the most obvious case of a heated pressure vessel, is now built up from welded steel plate. Plates of any thickness are now welded electrically, using either a multi-run technique, as shown in Fig. IV–8*a*, or a single deep pool weld on top of an initial sealing weld (Fig. IV–8*b*). In either case, the lower section of the weld is machined away, and the gap filled with fresh metal, as shown in Fig. IV–8*c*. These welds are now photographed by X-ray methods, and any flaws are machined out for rewelding. A joint which is found satisfactory will have an accepted strength of at least 90% of the plate strength.[7]

When the vessel has to be pierced by a number of holes, as in water-tube boiler construction, building up from heavy sheet is probably the only way to give a satisfactory construction, but the chemical industry is making increasing demands for large reaction vessels, in sizes up to 4 feet in diameter and 60 feet long, in which all entry ports are at the ends. Several alternative methods of fabrication have been tried. The simplest is that used for many years in gun construction—wire reinforcing on a relatively thin tube. This method leaves the problem of longitudinal stress untouched, and has had little application as a result. The logical development was to use sheet metal instead of wire for wrapping, when the combined thickness of the sheets would be available for both hoop and longitudinal stresses. The "multi-layer" method described by Jasper and Scudder[8] has found considerable application in the U.S.A., and is based on this sheet-wrapping principle. Alternatively, the round wire wrapping of gun technique can be replaced by interlocking grooved strips, about 3 in. wide, a process developed in Germany during the 1939–45 period.[9] A most interesting improvisation, described by Birchall and Lake,[10] showed how a thin steel tube could be reinforced by discs cut from thin steel plate to take the hoop stress, while a built-up frame from the same material held the vessel together longitudinally. All these ways of fabrication show the accommodating nature of steel as a material of construction. When a pressure vessel is to be jacketed, for heating or cooling, the "jacket" may reinforce the wall by fusion welding in spots to give a dimpled appearance, or may be formed from a coil and welded to the wall along its length.

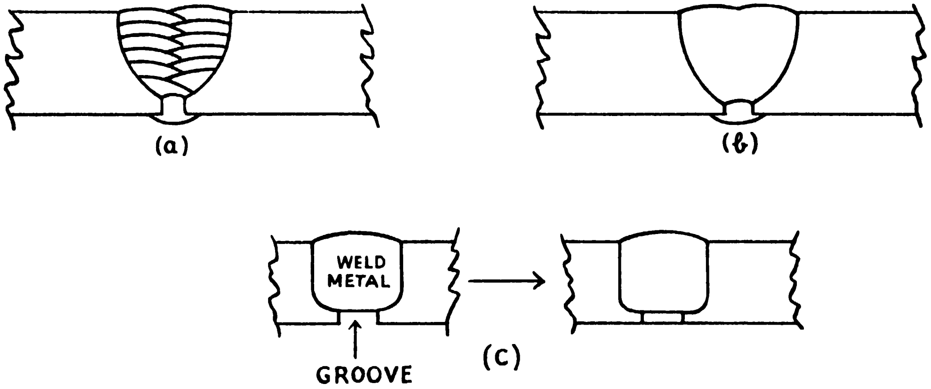


Fig. IV-8.—Fusion Welds in Heavy Plate.

The most common material for all forms of piping is now mild steel. Wrought-iron pipes, made by a special "puddling" process, used to be common, but are now becoming rare, at any rate in this country. A steel pipe is made up by methods which resemble closely those used in the manufacture of boiler plant. Long narrow sheets of steel are bent to a cylindrical form and the edges welded, either by a "lap" or a "butt" weld. These very long welds are commonly made by heating the metal to a welding heat and rolling under pressure, but electric fusion welding has also been employed. The most reliable, if most expensive, tubes are solid-drawn by punching a hole in the centre of a steel ingot, and then rolling or forcing through dies of gradually decreasing size until a seamless pipe of the required dimensions is obtained. From the point of view of corrosion resistance, solid-drawn methods are best, but lap-welded pipes with a forged weld are nearly as good. Butt-welded pipes made with a fusion weld should be avoided, as the seaming metal is almost certain to be of different composition from the wall, and electrolytic effects may set up a corrosion crack. The author recalls an extensive gas leak, leading to a minor explosion, which was traced to a weld crack in a wrought-iron pipe.

These steel pipes may be joined by threading the ends and screwing into special pipe fittings, generally made up in malleable iron. For heavy duty in chemical plant, the pipe lengths are commonly fitted with flanged ends, which allow for ease in dismantling. Suitable flange attachments have been specified, two of which are shown in Fig. IV-9*a*, and a joint of this kind is more adaptable to all pipe sizes than the compact union fitting shown in Fig. IV-9*b*. This latter is more rapidly tightened, and can take up a fair degree of misalignment in pipe lengths, but the locking nut is very clumsy when the pipe size exceeds about 2 in. Short screwed sleeves form the cheapest joint for pipes, but are not recommended unless the pipe-line is unlikely to be dismantled for any subsequent alterations. A number of proprietary jointing compounds are available for painting on to screw threads before a joint is made, but it is doubtful if they are any better than a thin paste of red lead and linseed oil, or shellac and hemp fibre for a permanent joint.

In all specifications for metal thickness an allowance is made for corrosion. As a rule this is given as $\frac{1}{16}$ in., but in a chemical plant, where external as well as internal corrosion is expected, a more generous allowance might be made. This is particularly necessary in steel construction, as against cast iron, where a generous thickness is always required by fabrication techniques. Many pieces of chemical plant are made up in such complicated form that once made they cannot readily be opened for inspection. A more generous allowance for possible corrosion should certainly be made in this case. A typical instance is the tube and shell heat interchanger, a simple form of which is shown in Fig. IV–10. The inside of the shell is very inaccessible, and the metal thickness for simple hydrostatic

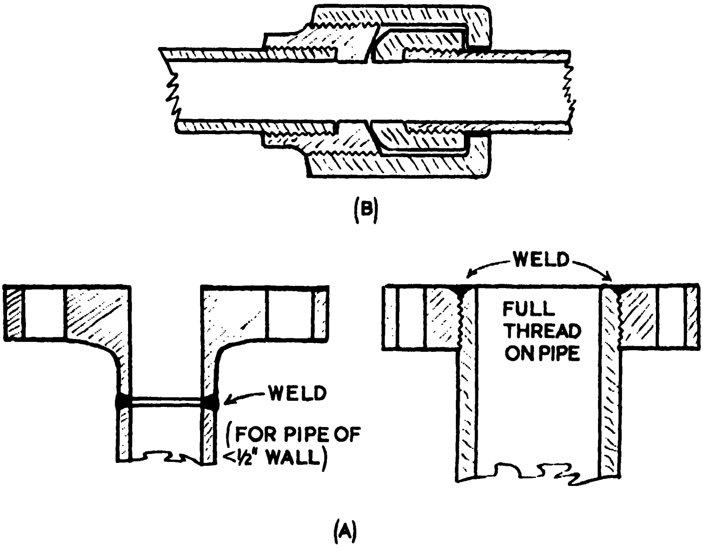


FIG. IV–9.—PIPE JOINTS.

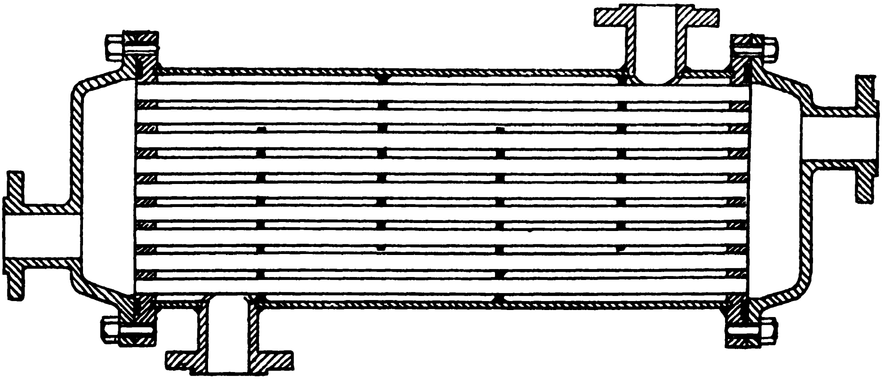


FIG. IV–10.—TUBE AND SHELL CONSTRUCTION.

hoop stress might be very small. If corrosive conditions are anticipated, then at least twice the normal allowance should be made. It may be noted here that the tube bundle, with the ends of each tube "expanded" into the tube plate (Fig. IV–11), is a commonplace of the chemical industry, and illustrates a very important form of metal-to-metal joint. The tube plate should ideally be of the same metal as the tubes, when a very good joint can be obtained with mild steel in annealed condition. A wide range of approved forms of joint, both for steel and for other metals, is set out in the provisional British Standard Code B.S. 1500 (1949) already referred to, while a comprehensive survey of American practice can be found in Siemon's handbook ("Manual for the Design of Ferrous and Non-Ferrous Pressure Vessels and Tanks" (3rd Edn.), Edwards Bros., Ann Arbor, U.S.A.).

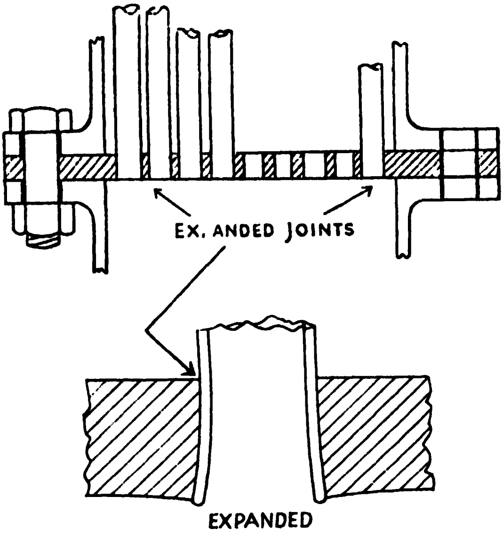


FIG. IV–11.—" EXPANDED " JOINTS.

The cost of ordinary steel, as plates or rolled sections, is determined to some extent by Government policy, and is subject to abrupt fluctuations. At the end of 1950, standard rolled-steel sections were costing £25 to £30 per ton, while sheets were from £30 to £32. Since then prices have increased steadily, and are now, at the end of 1952, about £5 per ton higher throughout the range. Plant fabricated from these "raw materials" will cost a minimum of £60 per ton, or about 6*d.* per lb., increasing as the plant grows smaller or more complex. The range might be from 2*s.* 6*d.* per lb. for simple plant weighing from 1 to 3 cwt., up to the minimum figure when weights of 1 ton or more are reached. These charges would be for stirred reaction vessels of straightforward construction, or standard pipe work, but attention is again drawn to the graph given in Chapter III (Fig. III–12). The weight of a cubic foot of steel is usually taken as 490 lb. (0·283 lb./cu. in.), but long tables of weights per unit area or length are set out in engineering yearbooks.

CORROSION RESISTANCE

It will be appreciated, from a study of the essential composition of steel, that the mechanism of corrosion will be essentially the same as that of cast iron, with the various constituents making for anodic and cathodic areas at the surface. As a consequence there is no great difference in the rates at which cast iron or steel oxidises and rusts in moist air, neutral water solutions, or damp soil. A chilled white iron or a martensitic steel would both be expected to give somewhat better resistance to incidental corrosion of the above form, but rusting would still proceed. Corrosive attack is checked by alkalies and promoted by acids, while, as with cast iron, a steel from iron and carbon only is not suitable for containing any dilute acid. The ease and cheapness with which steel can be made into all forms of plant has led to the development of protective coverings, to be described in a later chapter. These are primarily for dilute acids, and steel has no need for such protection when handling dilute alkaline solutions of all types. Except for the strong caustic alkalies, there are no limits to temperature or concentration.

Caustic Embrittlement

When steel is heated in contact with solutions of NaOH or KOH, it has been repeatedly observed that the plant may develop cracks, especially along the line of a joint. Riveted vessels are particularly subject to this insidious form of attack, as in Fig. IV–12, which has been responsible for many disastrous boiler explosions. The cracks are extremely difficult to detect, and may spread rapidly when a certain critical depth is passed. It is not necessary for the concentration of caustic alkali in the bulk of the solution to be very high —in the case of a typical boiler disaster[11] the concentration of NaOH probably never exceeded 0·1%. The physical characteristics of the hydroxide lead to concentration at a solid–liquid interface, especially where a crevice characteristic of a riveted joint may occur. Minute leaks from a vessel under pressure take the solution through to both sides of the joint, and drying out will leave a concentrated reagent. It has been shown that a cell of the form

Iron	Conc. $NaOH$ Solution	Dilute $NaOH$ Solution	Iron

gives a definite e.m.f., the iron in contact with the more concentrated solution dissolving as some complex ferroate. As the solution will only be concentrated in spots, these may act as small anodes, with the whole of the boiler surface acting as a cathode.

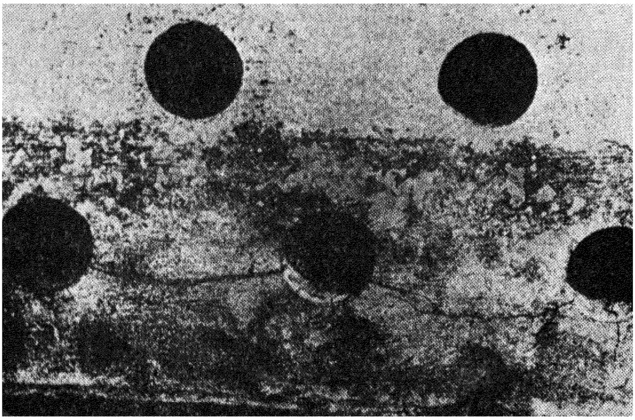


FIG. IV-12.—CAUSTIC EMBRITTLEMENT OF BOILER STEEL.

The normal conditions for intense local corrosion are set up and a primary crack develops. As a boiler shell is in a stressed condition, the usual effect of stress corrosion develops the primary crack still further, perhaps down lines of intergranular boundaries. This is the simplest explanation of caustic embrittlement, an unfortunate title in that the metal is not made brittle but is merely locally attacked. It is possible to corrode mild steel rapidly in boiling concentrated caustic soda solution, a typical specimen losing weight at a rate of 3500 mdd when immersed in 50% $NaOH$ boiling under a 25-in. vacuum. The steel crumbles under an intergranular attack very similar to that noted in boiler-steel embrittlement.

It would seem that the mechanism of attack is more complex than that set out above. A group of workers under C. H. Desch[12] suggested that two different types of attack could occur, one depending mainly on preferential solution of protective oxide skin, and the other on hydrogen penetration into the metal. This latter could really cause "embrittlement" but may not be so important as the former in boiler failure. The matter is still under dispute, and reference should be made to original papers for a fuller discussion.[13] It is of more interest here to cover the proposals made for prevention.

In the first place it is generally accepted that a high proportion of neutral salts, such as sulphates and chlorides, relative to the concentration of alkali, will inhibit caustic cracking. The concentration of alkali is given by the sum of carbonate and free caustic, as the former will hydrolyse in the boiler. Provided that the ratio of (sulphate + chloride)/(OH + CO_3) exceeds 3, it is debatable if any cases of cracking can occur.[14] The problem of testing is a difficult one, and embrittlement detectors, such as that devised by Schroeder and Berk[15] (Fig. IV–13) can only approach conditions in a typical boiler. Sodium nitrate, in amounts up to 40% of the free caustic present, has also been claimed to prevent attack,[16] while phosphate, added to prevent deposition of a sulphate scale, appears to check

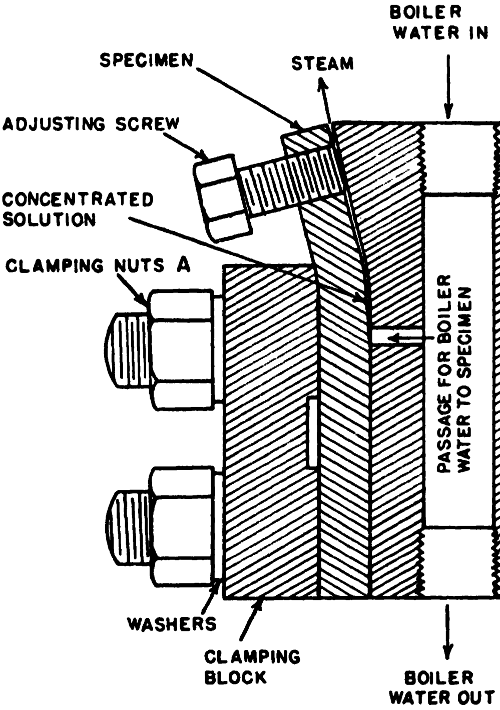

BOILER WATER IN
SPECIMEN
STEAM
ADJUSTING SCREW
CONCENTRATED SOLUTION
CLAMPING NUTS A
PASSAGE FOR BOILER WATER TO SPECIMEN
WASHERS
CLAMPING BLOCK
BOILER WATER OUT

FIG. IV–13.—EMBRITTLEMENT DETECTOR.
(After Schroeder and Berk) *loc. cit.*

cracking as well.[17] This latter may be due to control of OH′ concentration by the PO'''_4 ions. Claims[18] have also been made for organic inhibitors, such as tannin or quebracho, which may act as inhibitors for the discharge of H^+ ions, and thereby check solution of hydrogen and subsequent embrittlement. Undoubtedly a number of factors can and do check cracking very effectively, as many industrial boilers have a record of prolonged service which is difficult to match. The author has seen a battery of Lancashire boilers dismantled after thirty years' service in the London area—high-carbonate raw feed water—which were still in excellent condition and had only been found inadequate by more modern standards. These were riveted boiler shells, but the tendency to replace riveting by welding has perhaps diminished the number of sites at which embrittlement may occur. Apart from this specialised attack, the record given above shows how resistant mild steel can be to dilute aqueous solutions of neutral reaction.

Sulphuric Acid Corrosion

Rates of attack vary with H_2SO_4 concentration in very much the same way as with cast iron. Fig. IV–14 sets out the corrosive action that can be expected. It will be seen that a steel tank can be used for storing acid of 65% strength and over if the reagent is cold, but that any notable temperature increase will cause corrosion rates to go up sharply. When the acid is anhydrous, containing free SO_3, the mild steel is more rapidly attacked than a cast iron, but is not subject to cracking. As a result, it is widely used in contact plants for handling oleum (100% H_2SO_4 with SO_3 in solution). An unprotected steel tower, packed with acid-resisting stoneware shapes, can have a life of ten years[19] when such acids are being circulated for the absorption of SO_3 at temperatures around 50°, but it is more general to line with acid-resisting tiles. The hot oleum flows through cast-steel pipes to a cooler of hairpin form, with water trickling over the outside. Cast-iron pipes with an enamel lining are a possible substitute for conveying, but not for cooling, and are still subject to cracking. One of the problems in handling such acids in steel is that slight leaks will cause rapid attack from the outside as the spilled acid takes up water from the air. The same problem exists with the sulphur-bearing gases, which are inert to steel if dry and below 500° C. Again a slight leak, especially with an SO_3 mixture, can give dilute acid and external corrosion. Joints between pipes must be carefully made to prevent such seepage, but a simple asbestos gasket and properly aligned flanges are found satisfactory. In the layout of an oleum plant using pyrites the gases are normally purified by dust precipitation and washing in a lead plant, but after drying with concentrated sulphuric acid they can be handled in steel. The fans drawing air through the burners, and then reaction gases through the purification system, are of mild steel, and set at the outlet of the gas-drying plant. The gases under positive pressure are then forced through the reaction units and absorption towers.

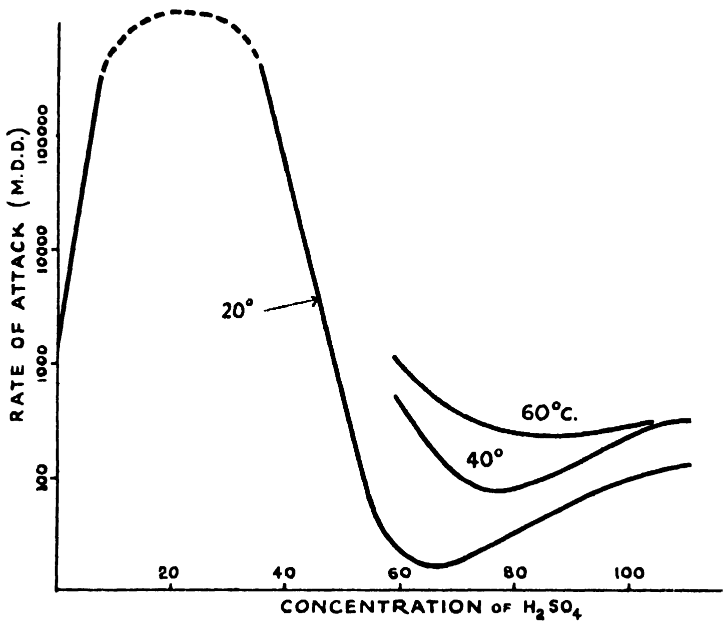


Fig. IV-14.—Attack of Sulphuric Acid on Steel.

Centrifugal pumps for the strong acid could be made in steel, but it is more convenient and cheaper to use cast iron, with perhaps a silicon-iron impeller.

General Behaviour to Acids

Nitric and hydrochloric acids will attack steel too rapidly for any normal use, whatever the concentration or temperature. The "passivation" of iron by concentrated nitric acid is too uncertain a factor to rely on for protection. Nitrating acids, of less than 25% of water and more than 10% of H_2SO_4, can be handled in steel. It is common practice, where dilute nitric acid is being recovered from fume for re-use in nitration, to mix with sufficient concentrated sulphuric acid to stabilise the mixture to cast iron or steel, and to pump or store in this form. There is no way of stabilising hydrochloric acid, and the general rule laid down on page 76 holds good.

Phosphoric acid will attack mild-steel plate at a rate of over 3000 mdd, but if combined with an inhibitor such as starch or glue the attack is much slower, and a protective skin forms on the steel which can inhibit later atmospheric attack. Such treatment, given by short immersion in the acid, or by a brushing process, is well known as a basis for painting or enamelling. The skin is not stable in the continued presence of phosphoric acid, and ordinary steel cannot be used either for pumping or storing the reagent.

Acetic acid, and all common organic acids, will be as active as phosphoric, but it is possible to refine mixtures of hydrocarbons containing acidic bodies in steel reaction vessels. Coal-tar, rich in phenols, has for many years been distilled in direct-fired pot stills made up from riveted or welded steel plate. Petroleum fractions are washed with concentrated sulphuric acid in steel washers of very considerable size, though lead-lined pots are preferred. A refined tar acid (phenolic type) almost free from neutral oils can be distilled from a mild-steel pot, or from steel pipes in a calandria or pot still, but the corrosion rate is high and the products are apt to be discoloured. Stainless-steel, Monel-metal, or nickel-clad equipment can with advantage be substituted, especially in the final condensers.

The action of dry chlorine or fluorine is small, as will be seen from the fact that both are normally transported in mild-steel compressed-gas cylinders. Damp chlorine gas will attack rapidly, but fluorine is not so active. In the industrial preparation of fluorine, electrolytic cells of mild steel deliver the gas through steel pipes, though Monel metal[20] is preferred for the valve systems. It is necessary to absorb HF in lead plant, as the dilute acid has too much action on steel, but a more concentrated acid (above 60% HF) can be stored in iron tanks. Bromine and iodine, both dry or in solution, cannot be handled in any form of steel.

Nearly all crude petroleum plant is made up from ordinary mild steel, as the oil forms a protective covering and inhibits ordinary atmospheric attack, while the active reagents present in the oil do not become dangerous until relatively high temperatures are reached. The most usual trouble in this field is attack by the decomposition products of sulphur-containing complexes, i.e. H_2S

or SO_2. It is unusual for these gases to be present in harmful quantities unless the oil has been heated to temperatures above 200°, or treated with active chemical reagents. Water is among these reagents, and for handling of moist "high-sulphur crudes" alloy steels are recommended (Chapter V). The pipe-still, in which a number of pipe lengths form a continuous conduit, can be built in seamless steel tubes for both tar and petroleum, but a low chrom-molybdenum steel gives better service, especially where pressures and temperatures are high.[21]

To sum up the general position of ordinary mild steel in the handling of acids, it is only in special circumstances, where a specific acid in high concentration protects by some form of anodic inhibition, that mild steel can give real corrosion resistance. As the cheapest and most mechanically reliable of constructional metals, available in almost unlimited supply, steel has been widely used with attack by chemical reagents accepted as a necessary evil. Naturally these circumstances have led to the development of many forms of protective coating, which are dealt with in a later chapter (Chapter XII).

Atmospheric Attack

This action follows the general rules laid down in the previous chapter. Anodic and cathodic areas can be formed by differential aeration, by heterogeneous surface structure, or by differential stress. An estimated life of ten years for mild-steel sheets of 0·05 in. in thickness has already been suggested for normal atmospheric weathering, and steel water tanks used for aerated town water will waste away at about the same rate, though this is a figure determined very largely by local conditions. A water from the Clyde Valley scheme, having a total of 20 parts of solid per 100,000, and a hardness of 1–2 parts, will rust 0·05-in. plate to destruction in less than five years, while Thames Valley water, with three times as much solid and ten times the total hardness, may give twenty years of effective life.

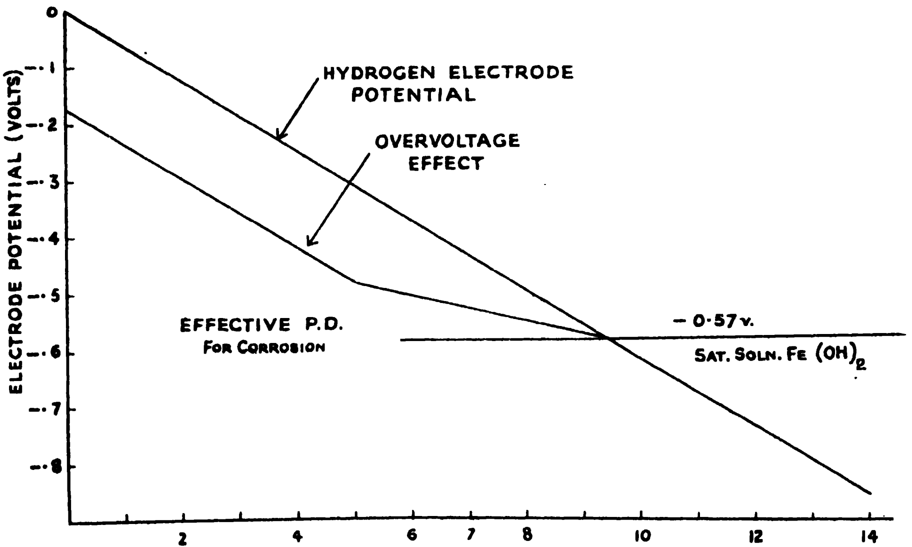
When sea water and air are involved, attack is much more rapid, and the great importance of such corrosion in these islands needs no stressing. The Institution of Civil Engineers have been for many years conducting tests on sites spread all over the world,[22] while the Iron and Steel Institute are running further tests in Great Britain.[23] A rate of attack of the order of 200 mdd, corresponding to a penetration of 0·04 in. per year, can be expected, but this is an overall rate, and corrosion is irregular, with local pitting. Conditions are, of course, ideal for corrosion, and will not normally be invited in chemical plants. A somewhat similar state of affairs exists in the case of crude-oil tanks where the oil is contaminated with sea water. This is common in the case of sea-borne oil, as the ship's tanks may be filled alternately with oil and sea water. Corrosion in the ship has been so serious that the plates are often covered with a layer of concrete, or rather neat cement. Alternatively, oxygen is excluded by filling the tanks with an inert atmosphere when empty. This latter step may be defeated by the fact that oxygen dissolves in many hydrocarbon products, and is carried into the reaction system as a solution. Where quantities of water are small, as in most land storage tanks, it may be possible both to absorb the water and introduce an inhibitor by adding fresh-burned lime. This has the advantage also that traces of acid from hydrolysis are absorbed. The sludge will be removed at intervals, of course.

The formation of tubercles of corrosion in pipe-lines has already been referred to (Chapter III, p. 64). A further cause for their appearance has sometimes been given as the action of iron bacteria, which flourish in faintly acid water (*p*H 5·8–7·2). When salts of iron and organic acids are present, the bacteria convert these to a characteristic sheath of ferrous and ferric hydroxide. In certain circumstances action can be amazingly rapid, and whole reservoirs may be turned dark red in colour in a few days. (Certain Biblical commentators have attributed the Mosaic curse which turned the Nile to blood to a similar outburst.) The action in a pipe is localised, with the bacteria gaining a foothold at certain arbitrary sites, from which a rust tubercle rapidly builds up. As the *p*H of the water rises to above 8·6 activity ceases completely.

These tubercles, once formed, will almost certainly act as centres of corrosion and pitting whenever oxygen is present in the water. Running water containing oxygen is described by Evans[24] as one of the most serious corrosion agents in industry, and attacks steel by the mechanism of incomplete aeration described in Chapter I, with pitting at unaerated portions of the surface. Even alkaline water, flowing along a steel pipe in which traces of debris have settled in the lower segments, can cause severe corrosion underneath the "protecting" fragments. The normal cooling systems of a large industrial plant involve a water-cooling tower, in which the water is circulated to become fully saturated with oxygen, followed by pumping through a number of cooling jackets, made almost automatically of steel, whatever be the nature of the inner wall. Clearly such water should be kept definitely on the alkaline side of neutrality and deliberate addition of a corrosive inhibitor might be considered.

The influence of dissolved solids, and particularly calcium, on corrosion rates has already been mentioned. It is interesting to note that the gradual change from lime-soda water softening to ion-exchange methods, which appears to be going on steadily through the years, will tend to introduce more corrosive conditions. The former process always left the water saturated with $CaCO_3$, and containing no "aggressive" carbon dioxide. Now ion exchange, especially if carried to the logical extreme of demineralisation, will leave the water free from calcium, but quite possibly still holding appreciable amounts of carbon dioxide.[25] Such water, passing along steel pipes which are normally protected with thin layers of oxide, will remove the protective skin and steady corrosion will result. The so-called "Langelier Index" for the water will be negative, indicating dangerous conditions. This index, devised by W. F. Langelier,[26] is the difference in *p*H given by shaking a sample of water with solid calcium carbonate (marble dust). If the *p*H change is *positive*, defined as a fall in value during treatment, then the water was originally supersaturated with calcium carbonate, and is not likely to cause corrosion. No change indicates equilibrium, while a *negative* change, or increase in *p*H as more carbonate passes into solution, shows that aggressive carbon dioxide is present. Any water supply with a negative index of more than —0·5 should be treated with lime as a precautionary measure.[27] Calcium deposits are far less harmful and obstructive than the tubercles and rust deposits from corroded pipes. An alternative to treatment with lime is the use of calcined dolomite, containing both magnesia and residual calcium carbonate, while additions of sodium hexametaphosphate are claimed to inhibit attack by aggressive carbon dioxide, and at the same time prevent the deposition of calcium scale. Certainly the introduction of phosphate conditioning has greatly diminished all forms of corrosion trouble in boilers, as mentioned above.[17]

Were it possible to remove oxygen completely from cooling water and all aqueous solutions in contact with steel, then hydrogen overvoltage and similar phenomena would very soon check corrosion almost completely. Fig. IV–15 shows how the potential difference available varies with hydrogen-ion concentration and with hydrogen overvoltage at zero current. The potential (—0·57 v.) of (iron metal/sat. soln. ferrous hydroxide) is reached at a *p*H of 9·4, but rates of solution become very small long before this. It is, of course, common practice to remove air from boiler water before use, generally by flash evaporation *in vacuo*, but the last traces need a chemical reagent such as sodium sulphite for elimination. Closed cooling-water systems might be treated in the same way, were it not for the almost universal open cooling tower. The vacuum evaporation cooling processes necessary in tropical countries possess the advantage of avoiding this re-aeration, but the cost as opposed to an ordinary cooling tower will be very high. It is probable, therefore, that oxygenated water supplies must be accepted as a necessary evil.



(After Hillier, Trans. I. Mar. E. 1950, 62, 1)

Fig. IV–15.

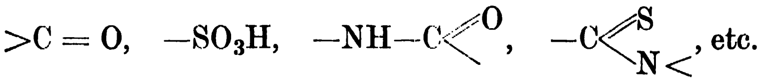
Inhibition

The deliberate addition of inhibitors to corrosive solutions has been practised most widely in connection with the acid "pickling" of steel. This process of steeping in acid removes from metal sheets the skin of oxide formed in milling, and leaves a clean metal surface for such operations as tinning, enamelling, or painting. The chemical action has been generally traced to reactions of the form

$$\text{Fe (Metal)} \rightarrow \text{Fe}^{++} + 2e \text{ (Anode)}$$
$$\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2e \rightarrow 3\text{Fe}^{++} + 4\text{H}_2\text{O} \text{ (Cathode)}$$

The various oxides of the scale, which may vary in composition from FeO to Fe_2O_3, are reduced to ferrous ions in solution, though much of the oxide coating may simply fall off through localised attack near the metal surface. So long as the anodic metal only dissolves in amounts sufficient to reduce the essential oxide of the scale, pickling is economic and no metal is really wasted. Any discharge of hydrogen at the cathode, $H^+ + e \rightarrow H$ (Gas-atomic), is not only uneconomic, but may lead to hydrogen absorption into the metal. Later processes such as enamelling will release this dissolved hydrogen within the body of the metal, causing cracking or blistering.

Now metallic iron in dilute sulphuric or hydrochloric acid will normally evolve hydrogen freely, and these acid conditions are required if the oxide scale is to be removed. As a consequence, hosts of "pickling inhibitors" or "restrainers" have been evolved to check this hydrogen liberation. Large colloidal molecules, such as gelatine or starch, were the first materials to be used, as mentioned in Chapter I, but have now been replaced with a number of patented organic reagents. These are sparingly soluble organic molecules, having a large "non-polar" body attached to a definite polar grouping of the type



$$>\text{C}=\text{O}, \quad -\text{SO}_3\text{H}, \quad -\text{NH}-\text{C}\begin{smallmatrix}\nearrow \text{O}\\ \searrow\end{smallmatrix}, \quad -\text{C}\begin{smallmatrix}\nearrow \text{S}\\ \searrow \text{N}<\end{smallmatrix}, \text{ etc.}$$

There seems no reason to doubt that all these agents attach themselves to a clean metallic surface, attachment being most marked at the cathodic points.[36] All reaction at such points of attachment will be checked by some form of steric hindrance. Attachment to oxide surfaces is much less marked, and cathodic reduction of these oxides can proceed without appreciable check.

When the oxide has been completely removed, action of the acid solutions will be much less marked. A reduction rate of 2500 mg./hr. is in fact reduced to less than 100 mg./hr. by the addition of typical inhibitors.[31] It would seem from this that the addition of traces of inhibitor (normally less than 0·1%) could bring about very considerable decreases in corrosion rate with almost all weakly corrosive aqueous solutions. The technique does not appear to have been widely adopted, however, and more attention has been paid to the action of such inorganic ions as chromates, phosphates,[32] or mixtures of the two.[33] The benzoates, introduced by Vernon and his co-workers,[34] can be improved by mixing with nitrites, and the mixture appears rather better than most sulphonated oils.[35] This field is being developed very rapidly and no final conclusion as to the relative merits of inorganic or organic inhibitors can be drawn.

IRON STAIN

It is notorious that iron surfaces tend to produce a colour in any materials brought into contact. Leather, in tanning operations, is extremely sensitive to iron, and will show a network of dark spots when curing is complete. Styrene will not give a colourless polymer unless the plant is made entirely from aluminium, even stainless steel being unsatisfactory, while salicylic acid sublimed into an iron chamber turns dark red instead of the pure white obtained with heavy tin-plate condensers. In some cases the effect is due to traces of an active oxide and will disappear if the plant is used continuously. A small pipe-still set to work on low-temperature tar gave such black distillates on first operating as to suggest that the still was "priming" or boiling over the pitch residue. After 48 hours the distillates were light brown and at the end of a week colourless. For intermittent working, with consequent reoxidation, an iron plant might have been impossible. A steel surface can catalyse the decomposition of diazonium compounds to a sticky tar at quite low temperatures, and at the other end of the temperature scale, prevent the formation of methyl alcohol from CO and H_2 by promoting the formation of methane. When the corrosive attack on metal is slight, the obvious solution is to use steel, as the reliable material of construction, and to cover with some more inert material, such as tin, copper, or chromium. The "clad" steels, or mild steel rolled into intimate contact with stainless alloy or some other metal, are the best examples of this combination, and will be described in due course. Iron salts are not toxic, but the discoloration given to many food products by mild-steel vessels militates against use even where no real attack on the metal occurs. It is almost impossible to prepare colourless salts in a crystalline form when mild-steel crystallisers are used, even though the salts may be crystallising from solution on the alkaline side of neutrality. All this indicates a certain degree of corrosion of the metal, and suitable preparation of the surface, or even ageing as above, can do much to diminish iron stain. It should always be borne in mind as a possible complication when using ordinary steel plant.

THE EFFECTS OF HIGH TEMPERATURE

As with cast iron, steel is rapidly attacked by air or oxygen when heated above 600° C. The curve of Fig. IV-16, showing initial rates of oxidation (gain in weight) brings this point out clearly. As the oxide skin thickens, some protection is afforded, but the nature of the iron oxides precludes any real inhibition. The ease with which fresh metal migrates into the oxide and the lack of firm attachment both rule out the possibility of using ordinary mild steel at temperatures above 500°, even when not under stress. A number of heat-resisting steel alloys, containing chromium or aluminium, are available, and will be mentioned in due course. Steam, the oxides of carbon, sulphur dioxide, and sulphuretted hydrogen are also destructive. It is possible to use steel for sulphur burners in which the interior temperature is above 600°, but the exterior is air-cooled and the metal temperature as a whole will not exceed 200° C.

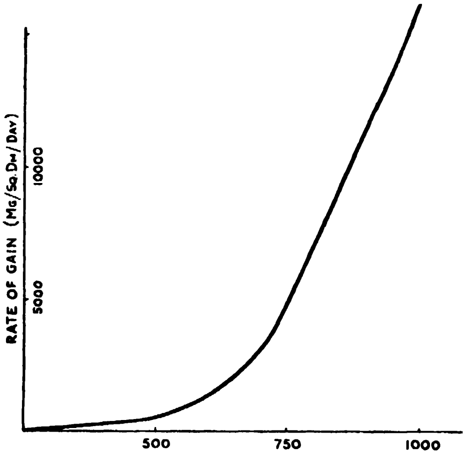


FIG. IV-16.—OXIDATION OF MILD STEEL.

It will be appreciated that mild steel is not a temperature-resistant material. The plot of strength against temperature (Fig. IV-6) suggests that it has little strength above 600°. At the same time, steel is often put under some small stress at more elevated temperatures, and it may be noted that a creep stress of 2 tons/sq. in. at 550° C. falls to 500 lb./sq. in. at 750°. (for 10^{-6} in./in. hr.). At the same time the metal grows more brittle, though it actually passes through a minimum value of impact-test figures at around 550°. When a steel is being chosen for such conditions, however, it is better to select one of the many "low"-alloy steels available for such work. The incorporation of 0·5% of molybdenum will double the normal creep stress, and performance is still further improved by the addition of 1% of chromium. Limiting factors then become the rate of attack of air or other reactant gases. Among these must be numbered hydrogen.

An ordinary steel will be attacked by hydrogen at temperatures as low as 150° if the gas pressure is high enough (about 200 atm.). The action appears to be through combination of the hydrogen with carbides, to form methane and iron-ferrite. This is largely on grain surfaces, and may cause intergranular fissures. Again the alloy steels will prevent such attack, perhaps by preferential formation of stable carbides, or by the stabilisation of austenite with no specific carbide phase. Titanium prevents attack in the first way, and a nickel-chromium alloy in the second. Perhaps the most severe conditions in the chemical industry for this form of attack are met in the synthesis of ammonia. The steel used for the catalyst chambers is a Ni-Cr-Mo alloy (Ni 2·5, Cr 0·6, Mo 0·4) which resists hydrogen attack at 400°-450° under a pressure of 250 atm. A fuller treatment of such steels is given in the next chapter.

WROUGHT IRON

This special form of low-carbon steel is seldom met with in chemical plant, and has, in fact, almost disappeared from modern industrial practice. It is made by heating pig iron in a reducing atmosphere at high temperatures until almost all the carbon has disappeared. As a result the iron melting-point goes steadily up until at the furnace temperature the mass is no longer fully molten. Then "blooms" of 100–200 lb. in weight are taken out and hammered while still hot to squeeze out the slag inclusions. The method leaves residual slag and oxide in thin layers, as shown in the microphotograph of Fig. IV–17. Such a structure has been claimed to check corrosion, but to the author's mind the almost pure ferrite structure is a possible cause for any extra resistance. There is some room for doubt in the claims[28] put forward for very long life, though many instances have been noted.[29] The rolled sheets made around 1850 were in wrought iron, and a gas-holder built from these was in steady use until destroyed in 1940. However, the cost of production is against the modern use of wrought iron, and it is likely to disappear, except perhaps for some traditional use, such as chain manufacture.

The modern substitute for wrought iron is a very low-carbon steel, made by normal methods and purified by over-oxidising with iron oxide. An "Armco"-type iron will have less than 0·015% carbon, with oxygen up to 0·2% as the chief impurity. The tensile strength will be as low as 21 tons/sq. in., but the extension on break will be more than 40%. With traces of copper (0·6%) this iron would appear to be very resistant to atmospheric oxidation. Whether it is much better than an ordinary copper-bearing steel is a matter of opinion. Reverting again to experience in the gas industry, the replacement of wrought-iron pipe by wrapped and bitumen-dipped steel pipes has been found to give a vast improvement in the working life of buried gas mains, but perhaps this is hardly a fair test.

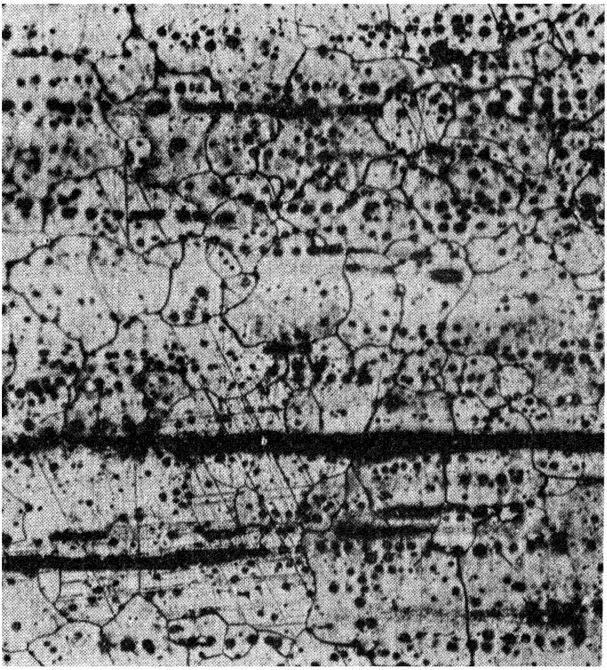


FIG. IV–17.—WROUGHT IRON (SHOWING SLAG INCLUSION).
(Courtesy of Dr. J. M. McLeod, Metallurgy Department, Royal Technical College, Glasgow)

REFERENCES

1. See, e.g., B.S. 487 and B.S. 1099.
2. Inglis, N. P., "Materials of Construction for Chemical Plant", *Soc. Chem. Industry*, London, 1950, p. 101.
3. Newitt, D. M., "Design of High Pressure Plant", Clarendon Press, Oxford, 1940.
4. Comstock, C. W., *Trans. Amer. Inst. Chem. Eng.*, 1943, **39**, 299; also Millar, B., *Chem. Eng.*, 1950, **57**, (1), 95.
5. Colbeck, E. W., and Mills, C. V., "Materials of Construction", p. 105.
6. But see B.S. 1500 (1949), Table 1.
7. *Loc. cit.*, Section 3(*c*).
8. Jasper, T. M., and Scudder, C. M., *Trans. Amer. Inst. Chem. Eng.*, 1941, **37**, 885.
9. F.I.A.T. Rept. 611.
10. Birchall, H., and Lake, G. F., *Proc. Inst. Mech. Eng.*, 1947, **156**, 349.
11. Foss Islands (York) Explosion, Official Rept., Aug. 1950, p. 10.
12. Desch, C. H., *et al.*, *J. Iron Steel Inst.*, 1941, **143**, 93.
13. See, e.g., *Trans. Amer. Soc. Mech. Eng.*, 1942, **64**, 397 *et seq.*; *Proc. Inst Mech. Eng.*, 1943, **149**, 63 *et seq.*; *Chem. and Ind.*, 1953, 180.
14. Hamer, P., and Colbeck, E. W., *Chem. and Ind.*, 1944, 163; B.S. 1170 (1947).
15. Schroeder, W. C., and Berk, A. A., U.S. Pat. 2283954 and 2283955.
16. Berk, A. A., *Ind. Eng. Chem.*, 1948, **40**, 1371.
17. Hillier, H., *Trans. Inst. Mar. Eng.*, 1950, **62**, 1 (Discussion).
18. But see Berk, A. A., *Chem. and Ind.*, 1953, p. 360.
19. B.I.O.S. Rept. 1632.
20. Porter, R. W., *Chem. Met. Eng.*, 1946, (**7**), p. 106.
21. Kirkhof, I. W., *et al.*, "Materials of Construction", p. 125.
22. Summarised by Hudson, J. C., *Rept. Corr. Com. Iron Steel Inst.*, 1934, **2**, 148.
23. Hudson, J. C., "Corrosion of Iron and Steel", Chapman and Hall, 1940.
24. Evans, U. R., "Metallic Corrosion, etc.", p. 317.
25. Parker, A., *Chem. and Ind.*, 1941, p. 867.
26. Langelier, W. F., *J. Amer. Water Works Assn.*, 1936, **28**, 1500.
27. See, e.g., Powell, S. T., *et al.*, *Ind. Eng. Chem.*, 1948, **40**, 453.
28. Hudson, "Corrosion of Iron, etc.", *loc. cit.*, pp. 81, 230, etc.
29. Speller, F. N. "Corrosion", 2nd Edn., McGraw-Hill, 1951, p. 66 *et seq.*
30. B.S. 1856 (1952).
31. Hoare, W. E., and Hedges, E. S., "Tinplate," Edw. Arnold, 1945, p. 53.
32. Parham, D. N., and Tod, C. W., *Chem. and Ind.*, 1953, 628.
33. Palmer, W. G., *Jnl. Iron Steel Inst.*, 1949, **163**, 421.
34. See, e.g., Vernon, W. H., and Stroud, E. G., *J. Appl. Chem.*, 1952, **2**, 166.
35. Ross, T. K., and Holness, H., *J. Appl. Chem.*, 1952, **2**, 250.
36. Hoar, T. P., and Holliday, R. D., *J. Appl. Chem.*, 1953, **3**, 502.

CHAPTER V

FERROUS ALLOYS

IN this chapter it is proposed to deal with alloys that are based on iron as the principal constituent, but in which the normal properties of an iron–carbon mixture have been substantially modified as the result of other additions.

CHROMIUM-NICKEL ALLOYS: THE STAINLESS STEEL GROUP

These are the most important of all ferrous alloys, and since coming into production some thirty-odd years ago have transformed the whole face of the heavy chemical industry, at least in so far as nitric acid and its derivatives are concerned. All contain chromium, and the majority nickel, as the principal alloying elements. Corrosion resistance is due primarily to the former, as will be seen from a glance at Fig. V–1. In order to produce this resistance, the chromium must be present as a solid solution in the iron. Reverting to the fundamental phase diagram for iron and chromium, the effect of adding chromium is to decrease the temperature range in which γ iron is stable. Ultimately the γ loop is closed, as shown in Fig. V–2. Now chromium is freely soluble in both α and γ irons, but it does form a relatively insoluble carbide or series of carbides; these follow the normal rule of being less soluble in α than in γ iron. Austenitic (γ) chromium alloys can only be obtained (Fig. V–2) when the chromium content is below 14%. If the mixture also contains more than 0·08% of carbon, these austenitic alloys harden to a martensitic structure on air-cooling. It is possible, however, to reduce the carbon content to below this level, when the steel cools to a much softer alloy, while the same effect can be obtained by tempering the martensitic steel at 750° to 850°, giving a normal pearlite structure. Such steels are not easy to weld, as heating–cooling reproduces a martensite structure, and an acetylene-welding process accentuates this change by increasing the carbon content.

The steels containing more than 15% of chromium are ferritic (α iron) in structure, very soft and malleable, and cannot be hardened by heat treatment. In fact, heat treatment of almost any kind, including that incident in welding, causes a growth of brittle grain structures which cannot easily be broken down. When the chromium content is increased beyond about 25%, a new form of iron—a sigma phase—appears. This is not of great importance in chemical plant work, although it has been suggested that local corrosion and cracking of stainless steels is sometimes due to the sigma phase being formed on prolonged heating in a range of 650°–900°. Such a treatment is steadfastly avoided for other reasons, as will be seen later.

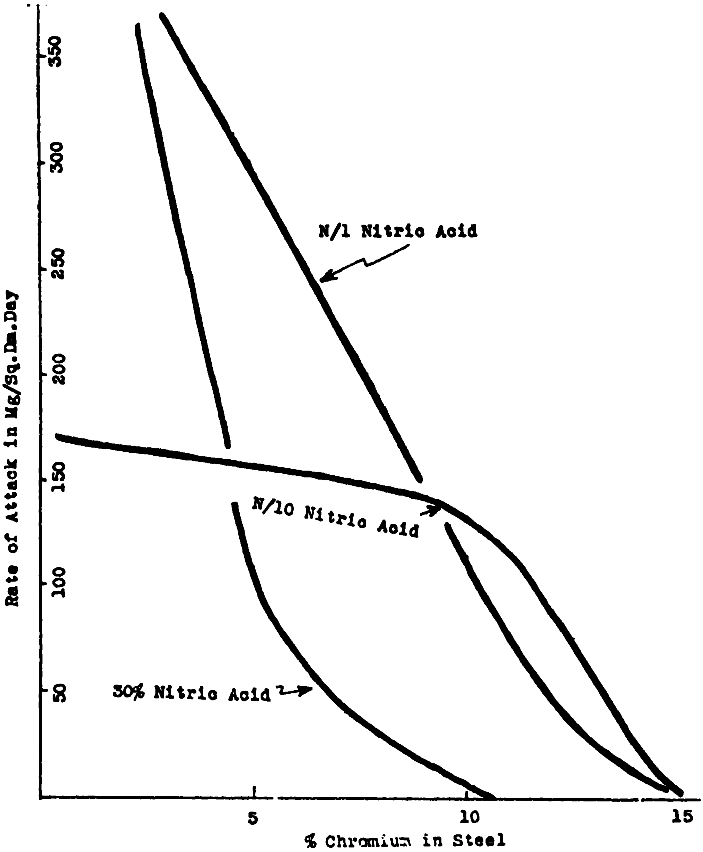


FIG. V–1.—EFFECT OF CHROMIUM CORROSION ON RESISTANCE.

The effect of nickel addition to an iron-chromium alloy is, as usual, to stabilise the austenitic form over a much wider temperature range. The curves of Fig. V–3 suggest the modifications caused by addition of nickel to an 18% chromium-iron alloy. It appears that at all normal working temperatures for metal fabrication

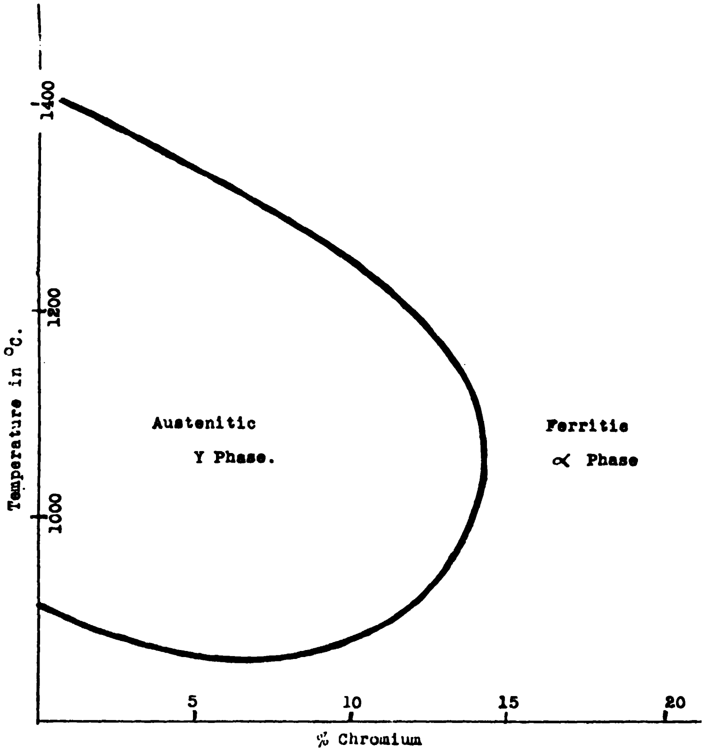


FIG. V-2.—EFFECT OF CHROMIUM ON AUSTENITE STABILITY.

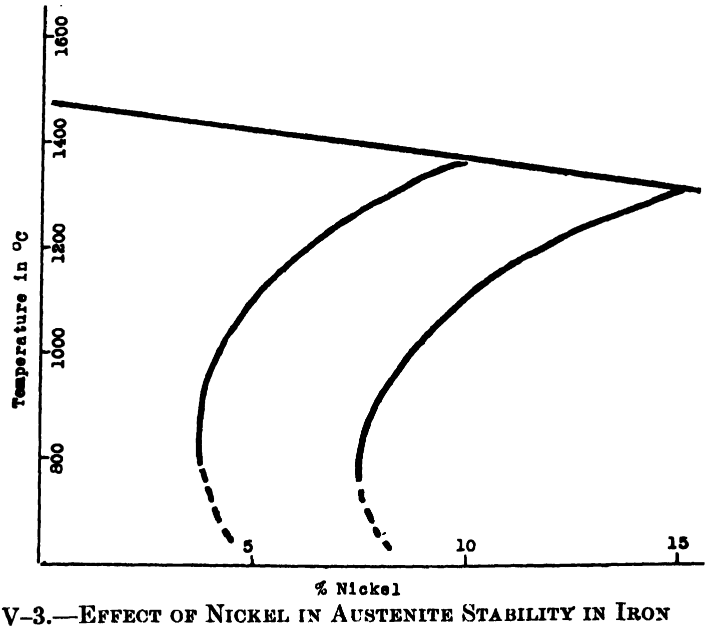


FIG. V-3.—EFFECT OF NICKEL IN AUSTENITE STABILITY IN IRON +18% CHROMIUM.

Left - Ferritic. *Right* - Austenitic. *Centre* - Indeterminate (usually Austenitic).

(900°–1200°) mixtures containing 8% of nickel are in the austenitic condition, with a consequent maximum solubility for carbon. This solubility drops very sharply with temperature, as will be seen from Fig. V–4. In order to avoid the possibility of carbide deposition. the carbon must be reduced to below about 0·02%—a very low figure and one that is likely to give troubles in casting or metal soundness. On the other hand, both nickel and chromium retard

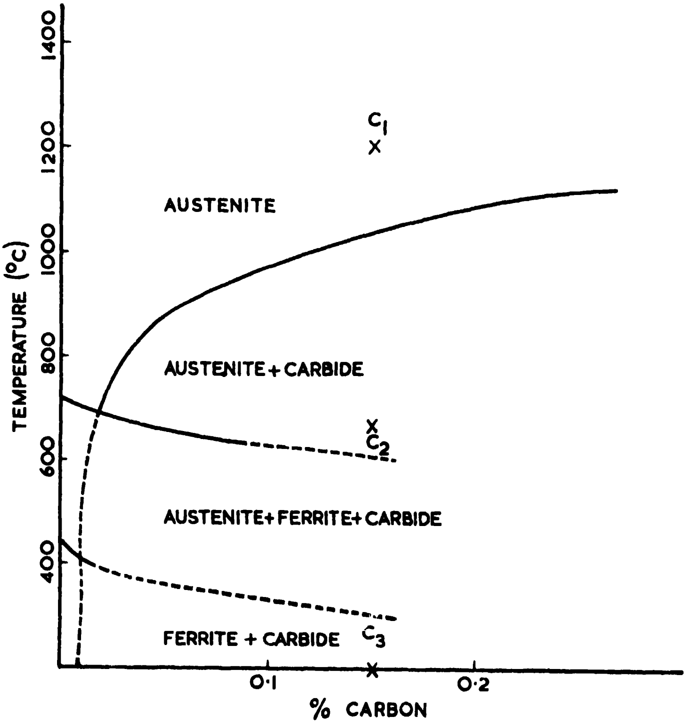
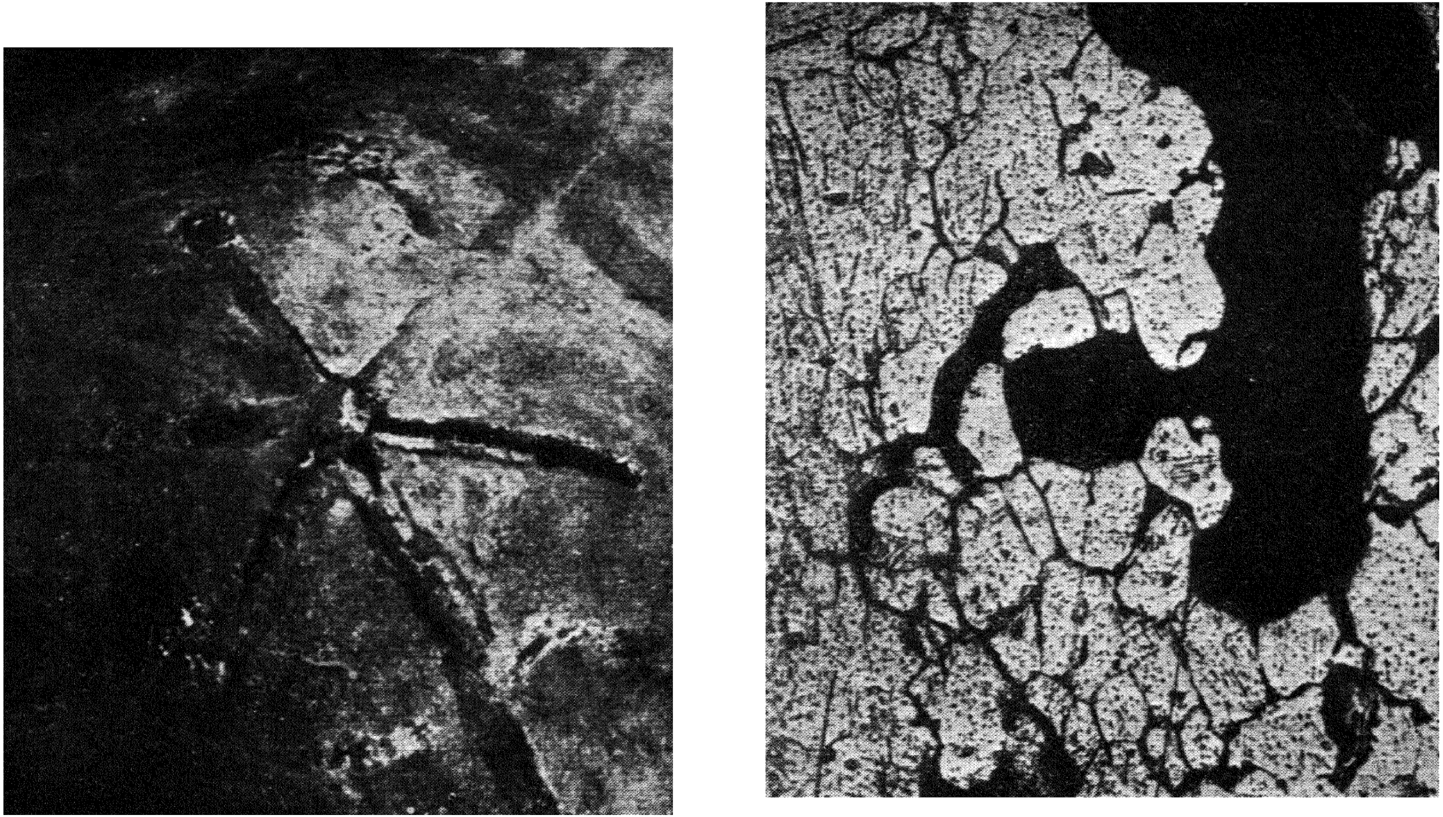


FIG. V–4.—PHASE DIAGRAM FOR 18Cr 8Ni STEEL.

the transformation of austenitic forms to a pearlitic form and will therefore tend to hold carbides in solution. It is easy to cool an alloy of composition represented by C_1 and retain the austenitic structure unchanged. The steel so formed is reasonably soft, ductile, and corrosion-resistant. Unfortunately, cold-working, if prolonged, tends to produce a mixture of carbides and ferrite, as represented by C_3, while heating for any length of time to a temperature between 600° and 900° will produce some such form as C_2—austenite and carbides. In both cases the bulk of the carbon will eventually be thrown out of solution as a carbide.

Chromium carbide in various forms, but chiefly Cr_7C_3, is much less soluble than the corresponding iron carbide and will therefore be preferentially deposited. Although the carbon present cannot carry down more than a small fraction of the total chromium, it can cause local shortages of this protective element. If a Cr_7C_3 is deposited, with a carbon content of 17·7%, then the loss of 0·13% of carbon from an alloy such as C_2 (Fig. V–4) will only entail the removal of 0·74% of chromium. But the carbon appears to migrate more rapidly to grain boundaries than the chromium, carbide is deposited in appreciable quantities, and the chromium-free iron left behind is subject to attack by any of the acids which are so inert towards a chromium-bearing material. When any stainless steel is welded, the actual weld metal is heated to melting-point and rapidly cooled, thus retaining the austenitic structure. A zone just outside the actual weld has been heated to within the critical range, and held there sufficiently long for some deposition of carbide to occur. Then this region is anodic to the rest of the steel, and in the presence of a corroding agent may be very rapidly attacked. The so-called "weld-decay" of stainless steel does, in fact, represent a very typical case of local breakdown in anodic inhibition. The photographs of Fig. V–5 show the unpleasant nature of this form of attack.

Clearly the obvious solution to this fabrication difficulty would be to heat the whole metal structure up to 1050°–1150°, according to the carbon content, and to cool rapidly enough to retain all the carbon in solution. This is not commonly a practical proposition for large chemical plant, and other methods must be sought. As will be seen from Fig. V–4, the permissible carbon content will fall to a very low figure if all carbide precipitation is to be avoided. It has been found, however, that the residual chromium will be adequate if the carbon is reduced to below 0·08%, and preferably to below 0·04%. Alternatively, if another alloying element is added, the carbides of which are still less soluble than those of chromium, then these will be preferentially rejected, and the chromium retained in solution. Such elements have been found in titanium and columbium (sometimes known as niobium). If these are added in amounts equivalent to the carbon present (4 to 5 times the carbon for Ti and 8 to 10 times for Cb), the weld-decay trouble is almost eliminated. Steels of this type are known as "stabilised" stainless steels, and are almost always used for chemical plant.



(*a*) Actual Size.

(*b*) Micro-photograph.

Fig. V–5.—Examples of "Weld Decay" in Stainless Steel.

(*Courtesy of Branch & Sweeten. Trans. Inst. Chem. Eng.*, 1949)

Both the additive elements for stabilised steels are in short supply, columbium more so than titanium. As a result, the latter has been widely used in Europe, while in the U.S.A. columbium is more common. In any case, welding rods for stainless steel will usually contain this less volatile metal; according to Branch and Sweeten,[1] nearly all the Ti in the rod will be volatilised, with 20% of the Cb and some chromium. If it is possible to heat-treat, the usual directions given are for heating to at least 1050° for an hour, followed by quenching to below 450° in less than three minutes. The increasing shortage of stabilising elements may make heat treatment, despite the cost and inconvenience, the most widely used method for avoidance of local corrosion.[2] It may be pointed out that even when chromium is kept in solution by stabilisation, a local precipitation of carbide has still occurred, and that weld decay in consequence is not fully eliminated. The advantage of heat treatment as set out above is that these carbide deposits are definitely dispersed. Another alternative which does not seem to have been very fully explored is an extensive cold-working (hammering) of the weld area. This would promote migration of the chromium and break up the localised carbide areas.

A special test for "weld decay" is usually incorporated into specifications for stainless steel. The terms of this[3] call for a test-piece to be heated for 30 minutes at 650° and then cooled in air. After such heat treatment the test-piece is immersed in a boiling solution of acid copper sulphate (111 gm. $CuSO_4$ + 98 gm. H_2SO_4 made up to 1 litre) for 72 hours. The metal should then stand bending through 90° over a radius of three times the thickness without cracking.

Quite apart from any development of local weakness, corrosion resistance in a metal demands as even a structure as possible. This means that an austenitic (or in some cases martensitic) structure is preferable to any mixture of carbides and ferrites. As martensite is inherently more unstable than austenite, the latter is to be preferred. Both chromium and nickel retard the formation of pearlite, but as mentioned above, increasing amounts of chromium decrease the temperature range in which an austenite is stable. Nickel can then be added to extend the range, giving a joint effect which is represented in Fig. V-6. As will be seen, the addition of nickel alone will stabilise austenite completely when about 20% is present. When chromium is also added, the slowing down of transformation to ferrite allows the use of less nickel at first. A minimum nickel usage is required in the neighbourhood of 18% chromium, and an 18/8 chromium-nickel alloy is persistently austenitic. When the chromium content rises much above 18% the nickel content must also rise to maintain suitable austenite formation conditions.[23]

Pearlitic stainless steels containing 12–16% of chromium and less than 2% of nickel can be obtained, with the possibility of easy hardening to a martensitic form, but they are not very common. Alternatively a ferritic stainless steel with 17–30% of chromium is easy to machine, cannot be hardened or tempered, and has excellent corrosion resistance. Mechanically it is rather weak and tends to develop a coarse grain structure at welds. In order further to increase the acid resistance of these alloys, certain steels now contain up to 3·5% of molybdenum. This addition is primarily designed to resist sulphuric, hydrochloric and organic acids, but the effect on physical structure must not be overlooked. There is some tendency to diminish weld decay, but not enough to allow the Cb or Ti to be eliminated. In addition, ferritic solid phases tend to form, without much effect on properties, but it has been stated[4] that the more unpleasant sigma phase develops if these Mo-bearing alloys are heated for long periods at 750°- 850°. In attempts to avoid this phenomenon, the nickel content has been increased to above 10%, and silicon, which plays some role in sigma-phase formation, reduced to the lowest possible figure. The normal steel structure always contains nitrogen, the action of which in austenite formation is obscure but apparently important. If nitrogen is completely absent, all austenite stability vanishes, and ferritic phases are always formed. The point is not of any practical importance, as nitrogen is difficult to eliminate from commercial irons. It is perhaps regrettable that a number of special trade names have been introduced to describe the various grades of stainless steel. The most popular of these are shown in Tables V–1 and 2, as set out by Branch and Sweeten.[1] A number of British Standards in this field have recently

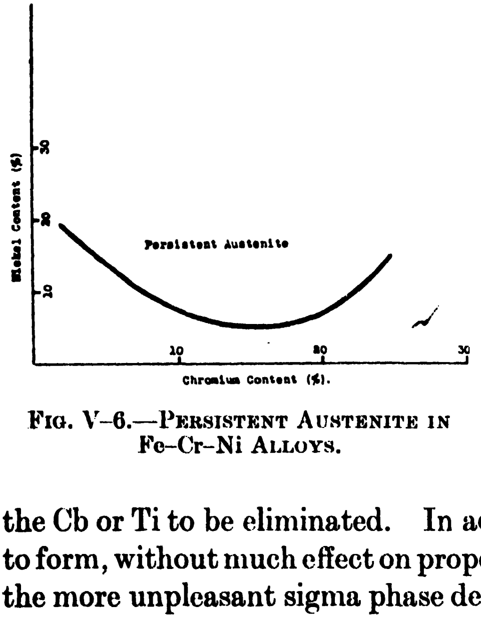


FIG. V–6.—PERSISTENT AUSTENITE IN Fe–Cr–Ni ALLOYS.

TABLE V-1. CHROM-NICKEL STEELS

Common Title:	18/8	18/8 Ti	18/10 Ti	12/12	Low C 18/8	18/8 Cb	18/10 Cb	18/8/1·5 Mo	18/8/3 Mo	Free 18/8 Cutting	25/12	25/20
British Standard: *	EN.58A (also 1501-801)	EN.58B (also 1501-821)	EN.58C (also 1501-821)	EN.58D	EN.58E (also 1501-801)	EN.58F (also 1501-821)	EN.58G (also 1501-821)	EN.58H	EN.58J (also 1501-844)	—	—	—
%												
C (max.)	0·16	0·15	0·15	0·16	0·08	0·15	0·15	0·12	0·12	0·15	0·20	0·25
Cr	17–20	17–20	17–20	11–14	17·5–20	17–20	17–20	17–20	17–20	17–20	22–26	24–26
Ni	7–10	7–10	9–12	11–14	8–11	7–10	9–12	8–12	8–12	7–10	11–14	19–22
Mo								1·5–2·5	2·5–3·5			
Ti		4 × C content (0·6% max.)								Cont. S, Se, Pb, etc.		
Cb						8 × C content (1·2% max.)						
Firth-Vickers	F.S.T.	F.D.P.	F.D.P. modified	D.D.Q.	F.S.L.	F.C.B.	F.C.B. (T)	F.M.L.	F.M.B.	E.M.S.	H.R. Crown max.	
Samuel Fox	S.F.20	S.F.22		S.F.21	S.F.620	S.F.26		S.F.25	S.F.35		R.F.31 (25/16)	R.F.X.R.3
Samuel Osborn	Evershyne B.S.	Weldshyne B.S.T.		B.S.2	Weldshyne B.S.M.	B.S.Cb		Weldshyne E.W.2	Weldshyne E.W.3–4	B.S.F.C.	I.K.	F.D.
Brown-Bailey	Anka H		Weldanka B	Anka M	Anka E		Weldanka C.B.	B.B.2 K	B.B.4 K	Weldanka K.K.	Hotspur F	Hotspur C
Edgar Allen	Maxilvry	Maxilvry A.W.P.		Maxilvry A.D.S.	Maxilvry	Maxilvry Cb			Maxilvry A.M.		Maxhete No. 2	
R. Thomas & Baldwin	P.E.L. or P.E.H.	P.E.T.		P.T.L.	P.E.L.		P.E.C.	P.M.L.	P.M.H.		P.25/12	P.25/20
Hadfield	E.R.A. C.R.I	C.R.I.S. H.R.2		C.D.D.							H.R.I.	H.R.3
Krupp	V.2 A	V.2 A extra		V.12 A supra	V.2 A supra			V.8 A supra	V.4 A supra extra			N.C.T.3

(After Branch and Sweeten, *Trans. Inst. Chem. Eng.*, 1949.)

* The normal specification for wrought steels is B.S. 970 (1947), with B.S. 971 (1950), as a complement. EN. numbers relate to this.

TABLE V–2. CHROMIUM STEELS

Common Title:	13 Chrome	13 Chrome Free Cut	S.80	17 Chrome	20 Chrome	27–30 Chrome
British Standard:	EN.56A (also 1503–613)	EN.56M	EN.57	-	- -	—
% C (max.)	0·12	0·18	0·25	0·12	0·35	0·35
Cr	12–14	12–14	15·5–20	15–18	18–22	25–30
Ni	1·0 (max.)	1·0 (max.)*	1–3	—	—	…
Firth-Vickers	F.I.	F.C.S.	S.80	F.I.17	F.I.20	Pyrista
Samuel Fox	S.F.10	S.F.610	S.F.18	S.F.17	R.F.11	R.F.12
Samuel Osborn	R.P.1	L.1	D.N.	M.B. 16/18 Cr	F.X.	E.K. 30/33 Cr
Brown-Bailey	Brearley A	H. K. Brearley	Two Score	Brearley C	LOw Score	Pyralloy 27
Edgar Allen	Imperial R.L.	Imperial R.L.F.C.	Imperial S.80	—	—	Maxhete No. 3
R. Thomas & Baldwin	P.K.L.		P.K.N.	P.K.1	P. 20	P.25
Krupp	V.5M		V.1M.	F.F 18	F.F. 25	—

(After Branch and Sweeten, *loc. cit.*)

* Also S, Se, etc.

been approved,[22] and parallel American steels are discussed in a series of articles[25] in "Chemical Engineering."

CONSTRUCTION IN STAINLESS STEEL

These alloys are generally available in sheet form, the sheets being 4 ft. to 4 ft. 6 in. wide and from 6 to 15 ft. long. These are much smaller than the largest sheets obtainable in mild steel, which means that welds will be more frequent and the cost of manufacture slightly higher on that account alone. Thickness is normally up to 1 inch, and reaction vessels are fabricated by rolling and welding. It will be seen that any cylinder of more than 4 ft. 9 in. diameter will need at least two longitudinal seams (cf. Fig. V–7a). This is an annoying factor which may be overcome by the use of stainless "clad" mild-steel plates, of which more will be said below. Bars and rods in all normal sizes up to 6 in. diameter are available, but no rolled sections except small angle forms—the largest being about 3 in. by 3 in. by ⅜ in. This means that any special girder or channel forms must be made up by welding angle or plate sections. Tubes are not easy to make in solid-drawn section owing to work-hardening effects, while a welded tube will have the characteristic difficulty of local corrosion unless carefully heat-treated after fabrication. The net effect is to add again to the cost of manufacture as compared to other metals of more tractable nature. On the other hand, wire of a wide range of thickness is available, with a considerable increase in strength due to the drawing operation. Ordinary 18/8 steel wire can be hardened from Brinell 135 up to 400, with a parallel increase in yield-point stress from 15·6 up to 116 tons/sq. in. The wires can be extremely fine and the author has seen experimental wire cloth with 350 wires to an inch of weave, giving a mesh aperture of the order of $\frac{1}{1000}$ in.

Castings in stainless steel are unusual, as the practice is to build up by welding. When casting is practised the temperature must be well above the melting-point, as the alloys are more viscous than ordinary steel or cast iron at parallel temperature ranges. A columbium-stabilised mixture must be used if any welding is to be carried out after casting; titanium would be lost by volatilisation. It is possible that some form of casting will be used in the future for repetition work, but the typical chemical plant will continue to be built up from plate sections. The preparation of suitable sections entails cutting of sheet, and normal flame-cutting in stainless steel is not possible owing to the formation of infusible chromium compounds. It is possible to use special fluxes, fed into the flame during cutting, which dissolve the chromium complexes, but the operation is never as simple and satisfactory as with ordinary carbon steel. Shearing and sawing both demand more power and give heavier tool wear, so that high-speed abrasive discs have been recommended. All machining, especially on the austenitic steels, is difficult owing to rapid work-hardening effects. Drilling of quite thin sheets can be made a major operation if the drills are not kept quite sharp and a steady cut taken.[20] This all adds to the cost of plant, and makes it necessary that simple forms should be sought.

Welding is the key operation in all plant fabrication, and must be carried out with great care, quite apart from any question of corrosion after-effects. An austenitic stainless steel has a coefficient of thermal expansion half as great again as mild steel, combined with much lower thermal and electrical conductivity. The welding metal has a higher melting-point, and this combines with the greater localisation of welding heats to give much more distortion. The stress thereby put on the cold joint is much greater, and thin welded sheets are very prone to buckle on cooling. Again, the carbon content of the weld metal must be low, for reasons set out above, and it follows that oxy-acetylene welding must be very carefully controlled to avoid an excess of fuel and consequent carbon pick-up. If a strongly oxidising flame is used, the obvious safeguard, then the weld will contain oxide inclusions which make it porous and brittle. As a result, only an expert can make a satisfactory weld with oxy-acetylene or similar methods, although it is quite a feasible proposition. Electric-arc welding is simpler, but the welding rod must be richer in chromium and columbium than the sheet metal. The effect of columbium on a titanium-stabilised sheet is not in any way deleterious, and as stated above titanium is lost from the weld-rod metal by volatilisation.

Coated electrodes are used, with a covering that gives fusible slag and protects the weld, while adding small quantities of stabilising metal. Long welds are usually made in short runs, with the plate edges left till last, though they should always be held in position by "tack" welds or clamps before the actual welding starts. Branch and Sweeten (*loc. cit.*) have described various methods of carrying out such welds. It is unusual to join thick sheets of half an inch and over by two or three runs, a number of light beads laid over each other being preferable, as in the older process for welding heavy steel sheet. The alternative submerged arc welding has been used with success, techniques being much the same as for steel sheets, but where titanium-stabilised sheet is welded, the heat volatilises sufficient titanium to give an unstable weld area. The process should apparently be confined to columbium-stabilised sheets, and is, of course, only practicable in large machine-shops. A process of inert gas screening during welding is being developed which seems to make a much sounder weld than the normal flux-screened process. An arc is struck between sheet and tungsten electrode, while argon or helium, in rates up to 8 litres per minute, forms a neutral atmosphere for the melting of a bare filler wire. Argon apparently gives better results than helium.[5]

Riveting of stainless steel is now very uncommon, as it is difficult to clean a riveted joint properly, and so many operations in this material need an easily sterilised and polished surface. Nevertheless, a riveted joint is not open to the usual troubles of carbide deposition, and can give quite good service in very corrosive conditions. Some of the earliest stainless-steel plant in the industry was of riveted construction, and much is still, after thirty years, in active service. The steel was unstabilised and might have fallen into pieces long since had the joints been welded. Other methods of jointing, such as brazing or hard soldering, while quite possible, are unsuitable for a material which is being used because of its inertness and corrosion resistance.

Arising from this last point, design should avoid any conditions which might promote reaction between plant and chemical contents. As an example, rubbing bearings should not be incorporated into any reaction vessel. A foot-step mounting for a stirrer shaft, when both are made in stainless steel, is almost certain to become a centre for corrosion, and the same is true of a gland exposed to acid fume. When such fittings are vital, it is preferable that the rubbing surfaces should be of two different grades (e.g. 18/8 and 18/8/3 Mo), following the usual rule that like metals should not "run" together. The improvement in valve life given by careful polishing has already been noted (p. 15), and in general all plant should be installed in "polished" condition. This is particularly necessary when all contamination of the material being handled is to be avoided. Design should take into account the need for polishing, even though this contributes to the cost. An ordinary descaled alloy-steel plate $\frac{1}{4}$ in. thick will cost about 25*s.* per sq. ft. (1952) and bright polish finish adds about 5*s.* to this basic charge.

Mild steel can be welded to a stainless-steel alloy, but the weld is very brittle unless a special welding rod is used, containing about 25% of chromium and 20% of nickel. By some such technique it is possible to prepare a stainless clad mild-steel plate. For instance, Barr and Erskine[6] describe the welding of mild steel to a thick stainless-steel ingot. The two are rolled out as a sandwich to give a mild-steel "cladding" on a thicker stainless steel. This is hot-rolled with a heavy mild-steel plate to pressure-weld the two mild-steel surfaces together, and finally the whole layered system is rolled to a suitable final thickness, with stainless steel covering the mild steel to a depth of about 0·03–0·1 in. This is not a very thin covering, and it has been suggested that clad steels need not be considered for any total metal thickness of less than $\frac{5}{8}$ in. It is demonstrably cheaper to build up a vessel in light-gauge stainless and support in a mild-steel framing, as shown in Fig. V–7. Nevertheless, $\frac{3}{16}$ in. plates have been covered with 0·035 in. of stainless steel and used with success. A composite billet with a stainless-steel core in mild steel has been rolled into lined tubes, but the process is expensive.

The ultimate tensile strength of annealed austenitic 18/8 steels is about 70,000 lb./sq. in., but the yield-point is only feebly marked and the proof stress approaches the ultimate strength. Work-hardening produces the usual increase, and a proof stress of 100,000 lb./sq. in. has been obtained. A further advantage of these chromium alloys is the retention of strength up to substantially higher temperatures, as shown in Fig. V–8. The 12–14% ferritic chromium alloys are not quite so stable as 18/8 steel, though British Specifications[7] make little or no difference between the strengths required at ordinary temperatures. According to Tongue,[8]

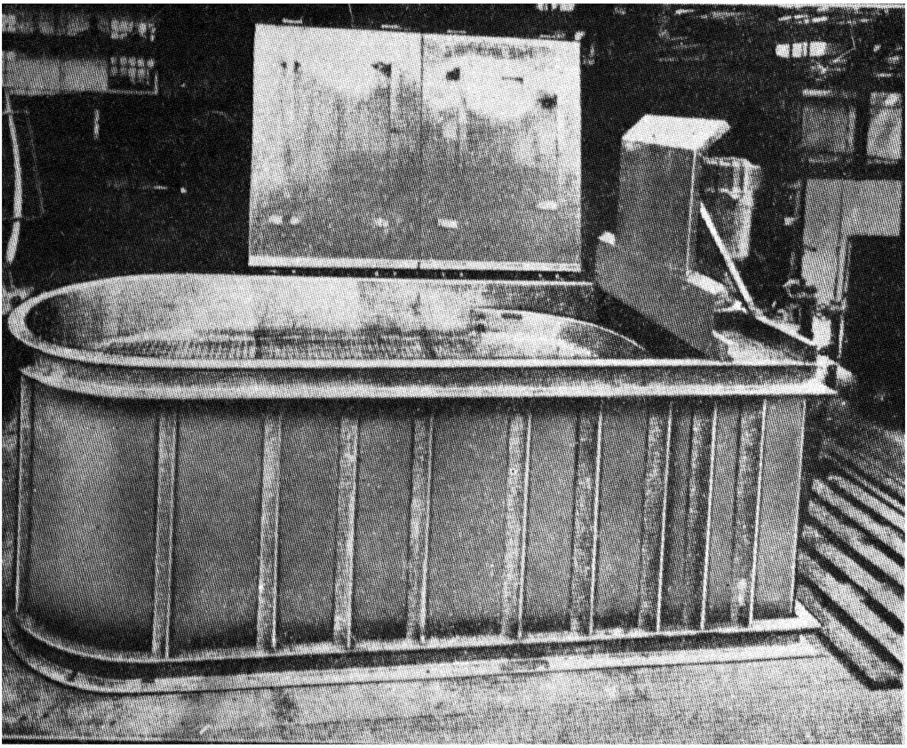


FIG. V–7.—STAINLESS-STEEL VESSEL WITH MILD-STEEL REINFORCEMENT.
(Branch & Sweeten, *Trans. Inst. Chem. Eng.*, 1949)

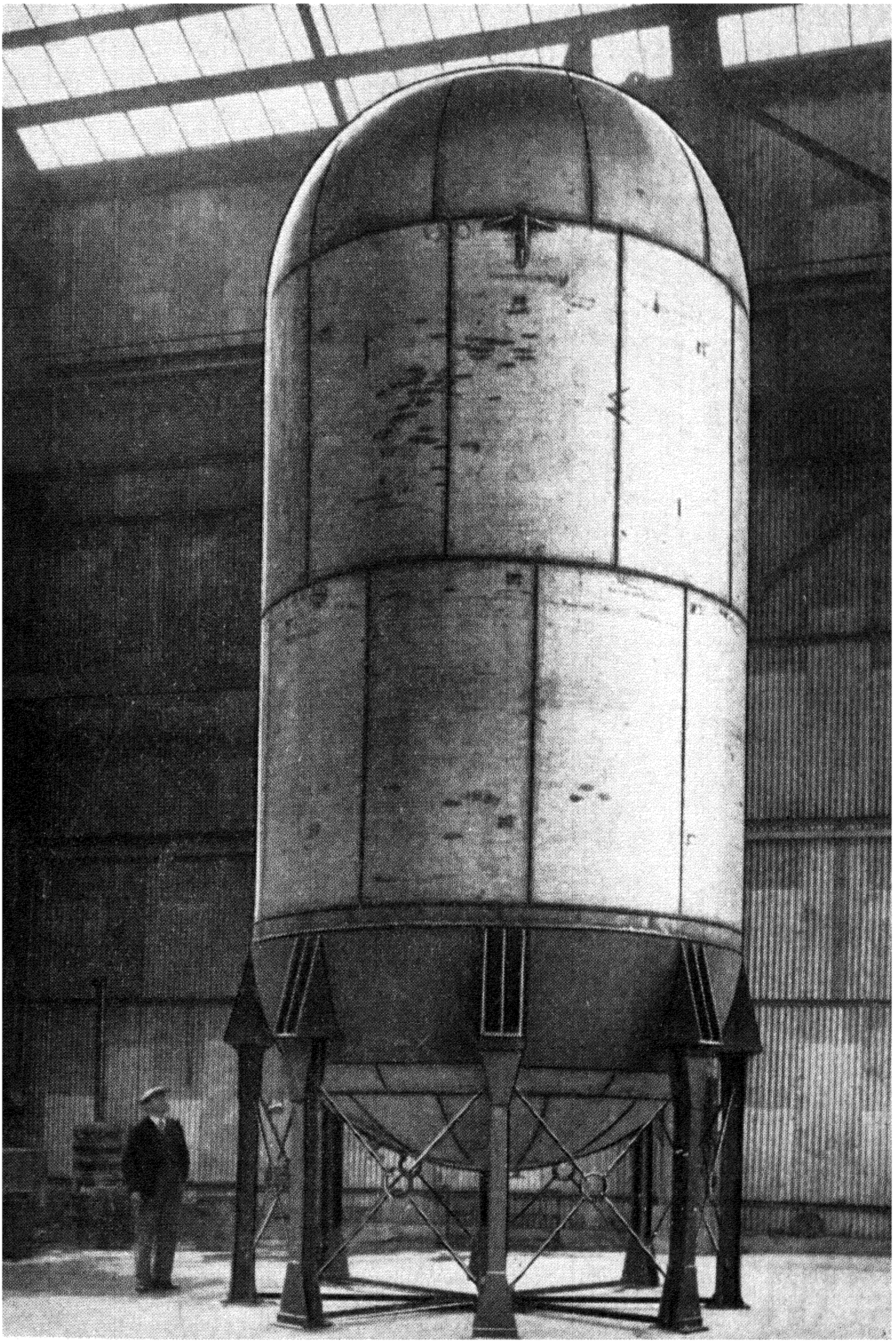


FIG. V-7*a*.—20,000-GALLON STAINLESS-STEEL TANK.

(*Courtesy of Thompson Bros.* (*Bilston*), *Ltd.*)

chromium is the active agent in conferring strength at elevated temperatures, and a 15% Cr alloy has twice the allowable creep stress of mild steel at 500°. The austenitic nickel-bearing steels are to be preferred, however, and have about the same safe load as the straight chromium alloy at a 50° higher temperature. A 12–14% Cr steel has about half the Izod impact value of the austenitic material, and is generally regarded as an inferior but cheaper substitute for 18/8 Cr-Ni alloy. The former is slightly more conductive at 12 B.Th.U. as against 8·5 for the latter (both figures are in B.Th.U./sq. ft. hr. ° F. per ft., at 15°–20° C.).[9] The "18/8/3" molybdenum alloy is almost identical with the ordinary "18/8" in physical properties.

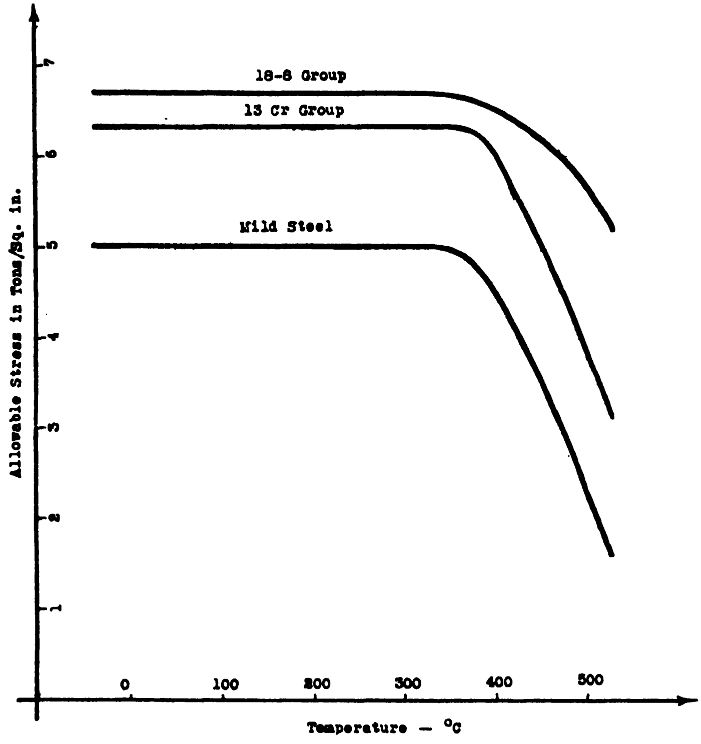


FIG. V–8.

(After Branch & Sweeten, *Trans. Inst. Chem. Eng.*, 1949)

It is more than usually difficult to formulate a price rule for stainless-steel construction, as any emergency conditions produce an immediate shortage, and supplies are then governed by Government decree rather than by any rule of supply and demand. It is normally reckoned that stainless-steel plant costs three times as much as the same units in mild steel. In a typical instance coming to the author's notice in 1951, spheres for liquid methane gas storage, 43 ft. in diameter, cost £31,000 in an 18/8 alloy as against £12,500 for ordinary mild steel. The subject was raised because of cracking in a mild-steel sphere, which initiated a gas leak and a disastrous explosion. As mentioned previously, austenitic stainless steel is not so subject to this low-temperature embrittlement. Costs cannot be notably reduced by the use of stainless clad steel, which appears to cost at least 60% as much as the ordinary alloy, and gives more difficulty in manufacture owing to the double welding always required—one for mild-steel backing and one for the surfacing alloy. The price of nickel and chromium is climbing steadily, and the cost picture may change in favour of clad plate in years to come. At present the best way to diminish the plant cost is to specify the thinnest practicable plate, and to reinforce this with a steel cradle, as stated above.[23] If the lining is specifically attached to the rigid frame it may be liable to stress corrosion at these points of attachment. Pipe-joints need not have the entire flange made in alloy; the ends of the pipes can be belled out and turned over in small diameters, or a very light flange plate welded on in larger pipes. These ends are backed by a mild-steel flange of normal thickness, which takes up the bolt stresses, using the two thin alloy flanges and a suitable gasket to make the final joint. No matter what care is taken to reduce the amount of alloy steel employed, stainless-steel plant is always likely to be expensive.

CORROSION RESISTANCE OF STAINLESS STEELS

All these alloys resist corrosion by virtue of an oxide film containing notable amounts of chromium. If this skin is not formed, the metal corrodes as rapidly as ordinary mild steel. Fig. V-9 illustrates tests by Forrest *et al.*, in which a carefully descaled metal was exposed to aerated water.[24] It will be seen that both ferritic and austenitic stainless steels absorbed oxygen as rapidly as mild steel at first, but the rate fell off rapidly as the film formed. Incidentally, the descaling was carried out by 10% hydrochloric acid, which illustrates again that hydrochloric acid cannot be handled in iron plant; a possible exception exists in the case of molybdenum-bearing alloys, as will be set out below. The film of oxide is an anodic inhibitor, and any local breakdown will lead to intense local corrosion. The phenomenon of "weld decay" is an illustration of this weakness.

In view of the importance of surface conditions, care must be taken to see that the steel is properly prepared, with an even film. Polishing, carried out under ordinary atmospheric conditions, acquires a new importance as ensuring that an even film of oxide covers the entire surface, and has been shown to give a high chromium content in this skin.[10] The mill scales left by rolling are inadequate and even dangerous, as the metal below a layer of loosely attached oxide may be in active condition. Pickling of the metal sheets to remove this scale calls for the use of very active acid baths. The most normal is a 10% HCl, 3% HNO_3 solution, with a trace of inhibitor, but a 15% HNO_3 containing about 0·5% of HF has been used. Both these baths also put on a fairly even oxide film, but it is always desirable to polish the steel after fabrication. When the plant is to be used in "reducing" conditions which cannot allow a damaged oxide film to be repaired, it may be worth while to pretreat with boiling dilute HNO_3 and to repeat this treatment from time to time. The enormous success of these alloys in dealing with all sorts of corrosive solution should not be allowed to obscure the fact that, like aluminium, resistance depends essentially upon a surface skin a few molecules thick.[26]

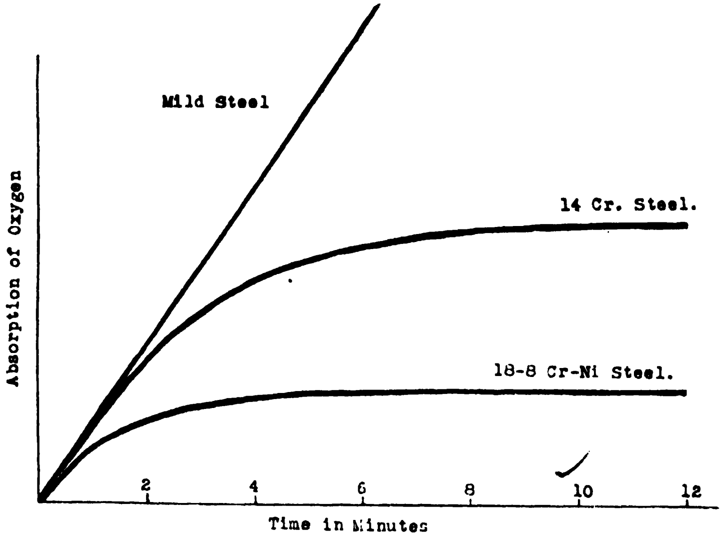


FIG. V-9.—INITIAL CORROSION RATES OF ALLOY STEELS.
(After Forrest *et al.*, *Ind. Eng. Chem.*, 1930, **22**, 1197)

Nitric Acid

The present-day nitric acid industry is built up on a foundation of stainless steel. These mechanically reliable materials are almost unattacked by nitric or nitrous acids of any concentration at any temperature. A possible exception might be made for acid of above 95% HNO_3, for which aluminium is to be preferred, but even this acid can be pumped, piped and stored with ordinary 18/8 steel plant. As a typical example of the use of this alloy, consider the absorption of nitrous gas from ammonia oxidation under pressure. The gases in admixture with air leave the heat-exchangers (also in chromium alloys) at about 600° and 150 lb./sq. in. They are cooled in water-sprayed 18/8 steel pipes and then enter the base of a bubble-cap tower, which may be from 6 to 8 ft. in diameter and 60 ft. high. These towers are built entirely from a stabilised steel, and are welded up *in situ* from cylinders about 4 ft. high, each section containing two or more bubble-cap trays with cooling coils immersed in the liquid. Each cooling coil passes through the outer wall of the tower, which may have up to fifty double pipe-ends welded into place. The gas mixture meets a descending stream of distilled water which is slowly converted into a 60% HNO_3 solution. Towers of this kind have worked almost continuously for ten years with no major repairs or leakage, despite the fact that any heat treatment after welding up is quite out of the question. In another process for acid manufacture, NO_2–water mixtures are converted by oxygen gas to a 96–98% HNO_3. The temperature rises to 150° and the pressure to 1000 lb./sq. in. during the reaction. A large autoclave, 3 ft. in diameter and about 30 ft. long, is used, built up from stainless alloy steel. The very searching effect of the concentrated acid is partly resisted by an aluminium thimble liner, but it is not possible to isolate the autoclave entirely. In one plant known to the author there was no disabling attack on the autoclave and valves over a five-year working period.

These plants were making nitric acid from ammonia, and traces of chloride were rigorously excluded, as will be seen from the reference to distilled water for the absorption tower. The "natural" nitric acid from nitrates is seldom met with nowadays, but would need to be handled either in silicon iron or non-metallic materials. Perhaps the molybdenum steels could be used, but the matter is open to doubt.

Sulphuric Acid ✓

This acid is much more corrosive than nitric and it is conservative to regard the 18/8 or 12–14% chromium steels as no better than ordinary mild steel in their resistance to H_2SO_4 concentrations of between 5% and 65%. A freely aerated dilute solution of this acid has little action on stainless steels, but any differential aeration may lead to rapid local corrosion. The relatively increased resistance under aerated conditions leads to "accidental" corrosion, when a plant is standing idle, being much lower than with mild steel. Pipe-lines conveying concentrated acid may be allowed to drain during such periods, and an acid surface diluted by moisture from the air above. Then a stainless-steel pipe will be relatively unaffected, while mild steel will be deeply pitted. For concentrated sulphuric acids of above 65%, there is little to choose between ordinary mild steel and the alloys under review, with the exception of molybdenum complexes. The stainless steel containing 3% of this element is definitely more stable in the presence of H_2SO_4, and has been claimed to resist all strengths up to a temperature of 60°, with corrosion rates well below 100 mdd. As this is a costly alloy, corrosion rates must be very low, or mechanical advantage very great, before molybdenum-bearing steel is substituted for lead in this field. ✓

As with ordinary steel, mixtures of nitric and sulphuric acids are more inert than either taken separately. Cooling coils in 18/8 alloy have been used in nitrators with a wide range of acid concentration and strength, and have given very long life in these conditions. The protective film is quite tough enough to withstand the alternate use of cold water or steam, and the tubing is far more rigid than lead of much greater thickness. This is an important point when stirring a fairly viscous slurry at high speeds. The nitrator vessel proper is normally made in cast iron, but has sometimes been built in 12–14% Cr steel. Such construction has the advantage of cheapness as compared with "18/8", and although slightly less resistant as a rule, is quite satisfactory for this particular work.

Other Acids

Phosphoric acid is normally reported to be without action on any of the steels in the cold, and not very active at boiling-point, although corrosion rates of 700 mdd for boiling 60% H_3PO_4 appear to put 18/8 alloy out of the question as a constructional material. There are commonly two grades of phosphoric acid available, a "crude" made by reacting phosphate rock with sulphuric acid, and a "pure" made by the absorption of P_2O_5 in water. The latter is definitely the more corrosive of the two, and ordinary "18/8" is considered suitable for the crude acid. For hot concentrated pure H_3PO_4 solutions only the molybdenum-bearing steel is suitable, though very high concentrations are liable to attack even here at uneconomic rates. Lead may be better and cheaper for the crude acid, while a special high-nickel alloy has been recommended for the pure solution.[11]

Organic acids have little or no action on the stainless steels in the cold, but as temperature increases the passivating film may break down, and corrosion rates will go up suddenly. The molybdenum-bearing steels are very much better, being stable to boiling acetic acid of all strengths, and reasonably resistant even to boiling fatty acids, though Inconel is better for this service (see Chapter IX). Sulphurous acid, probably acting in an oxidising capacity, has no action on the alloys, even the 12% Cr being satisfactory for this reactant. Examples of weld corrosion have been noted with wet SO_2 gas. Hydrochloric acid, as usual, attacks all the steels.

Salt Solutions

The action of neutral salt solutions follows that of acids. Those which have any oxidising capacity are inert unless chlorides are present. The higher chlorides of multivalent metals ($FeCl_3$, $SnCl_4$) all attack, and as would be expected, the action is localised, with marked pitting and cracking. Neutral sodium chloride is not very active, and aerated sea water soon gives a passive film and no further attack. If marine growths cause the formation of unaerated areas, the steel will be attacked, and there is no toxic effect to check this growth, as in the case of copper. Neutral sulphates are almost inert, but traces of acid cause attack at uneconomic rates, at any rate for the 12–14% Cr and 18/8 alloys. On the other hand, nitrates and sulphites, except those of the heavy metals, are quite harmless. An 18/8 stainless alloy evaporator can concentrate to crystallising point the solution made by passing ammonia gas and nitric acid simultaneously into a reaction vessel of similar material, and the rate of corrosion is negligible whatever the *p*H of the solutions. Acid nitro-bodies such as T.N.T. can be washed free of a mixture of nitrating acid, and then purified by washing with sodium sulphite, using 18/8 steel vats, and the plant appears to work through several years with no need for any repair work at all. The hard inert surface of burnished plate offers no lodgment for crystal nuclei, and makes the material particularly suitable for the construction of crystallising plant. Thus the very large crystallisers of the Sindri factory in India,[12] forming NH_2SO_4 from the double decomposition of $(NH_4)_2CO_3$ and $CaSO_4$, were made entirely from stainless alloy.

Foodstuffs

Stainless-steel kettles are widely used for all types of foodstuff and beverage manufacture. They are easy to keep clean and sterile, which is a very important consideration when dealing with such delicate mechanisms as a special strain of yeast, and the mildly corrosive action of food acids is quite negligible. On the other hand, the surface of the metal is hard enough to resist erosion and mechanical wear. Much of the work in this form of industry is carried out by hand, with the possibility of careless tool-handling, and the alternatives of aluminium and copper show much more risk of accidental damage. Milk and milk products are particularly stable when handled throughout in these steels, whereas copper must be heavily tinned to prevent traces of the metal causing sour tastes. One exception to the stability of stainless steel with an oxidising agent must be mentioned—hydrogen peroxide of high strength is decomposed catalytically by these alloys. A very high-nickel alloy has been recommended for pumps, but it is probably better to avoid iron altogether (with lead and copper) and to rely on aluminium, as soon as the H_2O_2 concentration rises above about 10%.[13]

Alkalis

Alkaline solutions react in the same way as with mild steel, and there is generally no advantage in using the much more expensive alloy. Despite the presence of nickel, an 18/8 steel is rapidly attacked by boiling 50% NaOH solution, and all the phenomena of caustic embrittlement can be produced. It would not be expected that chromium-bearing alloys will be stable in the presence of strong alkali, and this has been borne out in practice.[20]

Petroleum and Coal Tar

Stainless steel fully shares the resistant qualities of mild steel towards these liquids, while at high temperatures the performance is much better. The severe corrosion caused in mild steel or cast-iron condensers by mixtures of tar acid and water can be checked, if not eliminated, by the use of stainless alloys, while the pipes of standard "pipe stills" are generally made from 12% Cr alloy, though the 18/8 steel is just as good. These pipes have to stand up to oil and vapour under pressure at 400–500°, and show negligible corrosion rates.

This brief outline of the extraordinary corrosion resistance shown by stainless steels can be supplemented by a series of charts published recently,[25] while two monographs on corrosion can also be consulted.[14, 15]

OTHER CORROSION-RESISTING CHROMIUM-NICKEL ALLOYS

The stainless steels for corrosion resistance have fallen into three main groups, the austenitic "18/8", the ferritic (and sometimes austenitic as carbon content dictates) "12–14% Cr", and the molybdenum-bearing 18/8 steels. On occasions, alloys with still larger proportions of nickel, chromium, or some other alloying element have been introduced for enhanced corrosion resistance. These may not have more than a fugitive existence, and many appeals have been made to avoid special alloys for the sake of a rather hypothetical improvement, as costs mount steadily with each alteration in a generally accepted specification.

The high-nickel alloy mentioned above,[11] and introduced in an extension of the Firth-Vickers group of steels as "254", is very similar to the ordinary molybdenum-bearing steels, except that the nickel content has been increased from 8% to 18%, with some additional copper and more titanium. Mechanical properties are almost identical with "18/8", but the resistance to all acids is improved, especially with sulphuric acid. Some very high figures are quoted for boiling-point corrosion, however, and there is still no comparison between the performance of "254" and a good silicon iron in this particular field.[27]

A fair number of 20–30% Cr, 20–30% Ni alloys have been made up, of which perhaps the American alloy F.A. 20 can be taken as example. This alloy, of the "Durimet" group, has a low carbon content, with 29% Ni, 20% Cr, 3·5% Mo, 4·0% Cu as the principal alloying elements. It will be seen that the ferrous content is less than 50%, and classification as a ferrous alloy is arbitrary. The metal is better than ordinary steels for hot strong $MgCl_2$ or the alums, while showing about the same resistance to acids as the "254" alloy. It has a border-line resistance to salts of heavy metals, hypochlorous acid, and wet H_2S gas. Clearly such an expensive material can only be used for pumps, valves, and other small parts, for which it possesses excellent mechanical properties.

HEAT-RESISTING FERROUS ALLOYS

The breakdown of mild steel, both by mechanical weakening and by scaling, severely limits its use above 450° C. On the other hand,

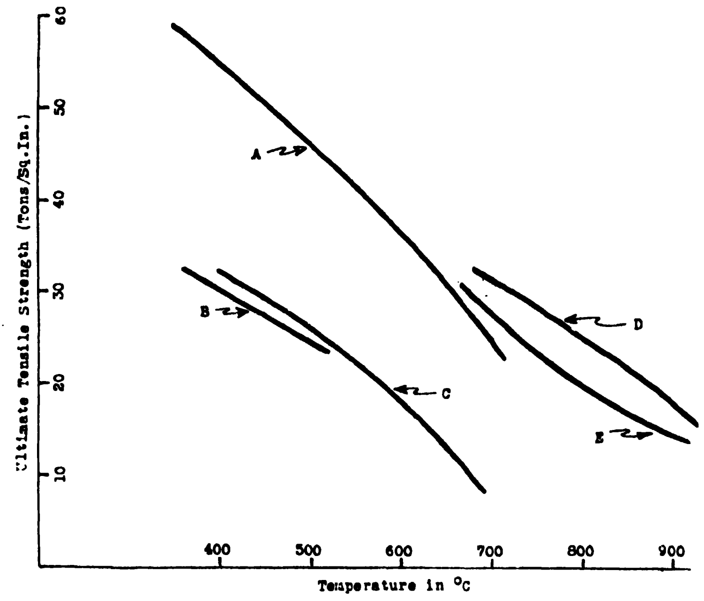


FIG. V–10*a*.—STRENGTHS OF HEAT RESISTING ALLOYS.

incorporation of small amounts of alloying material raises the temperature ceiling very considerably. The added strength also allows of much lighter construction at temperatures in the range 250° to 400°. The most usual additives are molybdenum, chromium, silicon, and nickel, but again a very wide range of alloys has been manufactured.

One of the most typical of these is a 3% Cr, 0·6% Mo alloy which is made under specification[16] to have a 0·1% proof stress of more than 45 tons/sq. in. Such a steel is capable of withstanding a working stress of 12 tons/sq. in. at 300°, and can be prepared in large ingots of 250 tons in weight. From these the very large pressure vessels required as a single forging can be made, up to 5 ft. in diameter with 6-in. walls. The strength of such a steel is very considerable up to 700° C., but if exposed to air at these temperatures, it would tend to scale rather badly. The resistance to scaling increases steadily with the chromium content, though the actual strength does not vary much. A 5% Cr alloy will not scale at 600°, and a 28% Cr is practically unattacked at 1000°. Certain properties of these steels, given by Colbeck and Mills,[17] are summarised in Fig. V–10 and Table V–3.

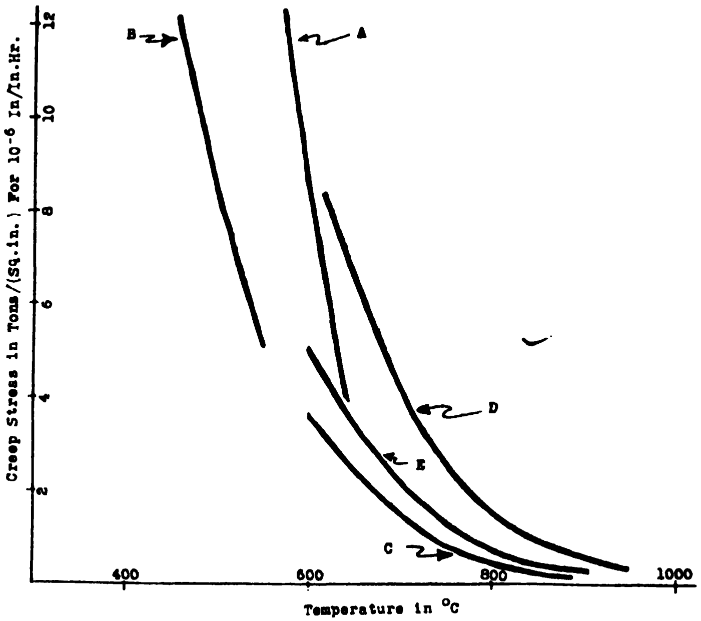


FIG. V–10*b*.—STRENGTHS OF HEAT RESISTING ALLOYS.

TABLE V–3

Steel	Composition								Resists Scaling to
	Cr	Mo	Ni	V	W	Si	Mn	C	
A	2·6	0·6	0·25	0·84	0·5	0·40	0·30	0·21	—
B	5·0	0·5	—	—	—	0·30	0·50	0·15	600° C.
C	28·0	—	—	—	—	0·6	—	0·35	950° C.
D	21·0	—	7·0	—	4·0	1·5	—	0·35	900° C.
E	25·0	—	20·0	—	—	1·5	—	0·15	950° C.
Stainless Steels	—	—	—	—	—	—	—	—	Abt. 800° C.

So many of the high-pressure gas reactions requiring large reactors involve the use of hydrogen that the resistance of steels to this gas becomes a primary consideration. Mild steel is quite unsuitable, as stated in the last chapter, any temperature over 150° leading to methane formation and hydrogen solution in the metal. Again the presence of chromium is vital, as Inglis and Andrews[18] showed some years ago. The 3% alloy mentioned above is quite stable at 350°–400°, but will show some signs of attack at higher temperatures. If the chromium content is increased to 6% there is no sign of attack at 500°, either by decarburisation or by solution and embrittlement. However, the 3% alloy is quite good enough for most industrial applications, and is a much better alloy than the 6% Cr for all machining purposes. As the alloy content grows still higher, and the stainless range is reached, the liability to hydrogen embrittlement by solution increases again, but only slightly.

The heat-resisting steels are not easy to work mechanically and are prone to air-hardening on cooling. They can be cut, with especial care and sharp tools, but grinding may be necessary. Welding must be on a clean metal surface with a reducing flux, and the finished weld should be heat-treated by taking to 1000° and quenching in oil. Any coarse metal structure at a weld tends to promote hydrogen embrittlement, while the high-chrome alloys (C, D, and E) all form sigma phase on prolonged heating in the range 550°–950°. They may also give disappointing results in strongly reducing atmospheres, especially where sulphur is present.

Such alloys are expensive and are only used when temperature conditions demand, as in catalytic reactions at 600°–800°. Pots for molten salt baths, as used in metal tempering, must be made up from one or other of the alloys, generally high in nickel to resist the alkaline reactions of such salts as sodium cyanide. Again, the containers for "nitriding" ordinary steels (Chapter XII) have to withstand ammonia gas at 600°–700°, and are customarily made up in high-chromium metal. They may need heat treatment at intervals to remove sigma phase, but apart from this have an almost indefinite life. The rakes in a pyrites-roasting furnace must be strong enough to turn over a heavy powdered ore at temperatures which reach 900°, and at the same time be unaffected by gases containing sulphur dioxide in large quantities. Normally the surplus air is sufficient to stabilise the high-chrome alloys, and their hardness makes them proof against abrasion. Unfortunately, all these steels grow brittle in use, probably through the formation of sigma phase, and the teeth of the rakes, made from 2-in. square bar, break at intervals.

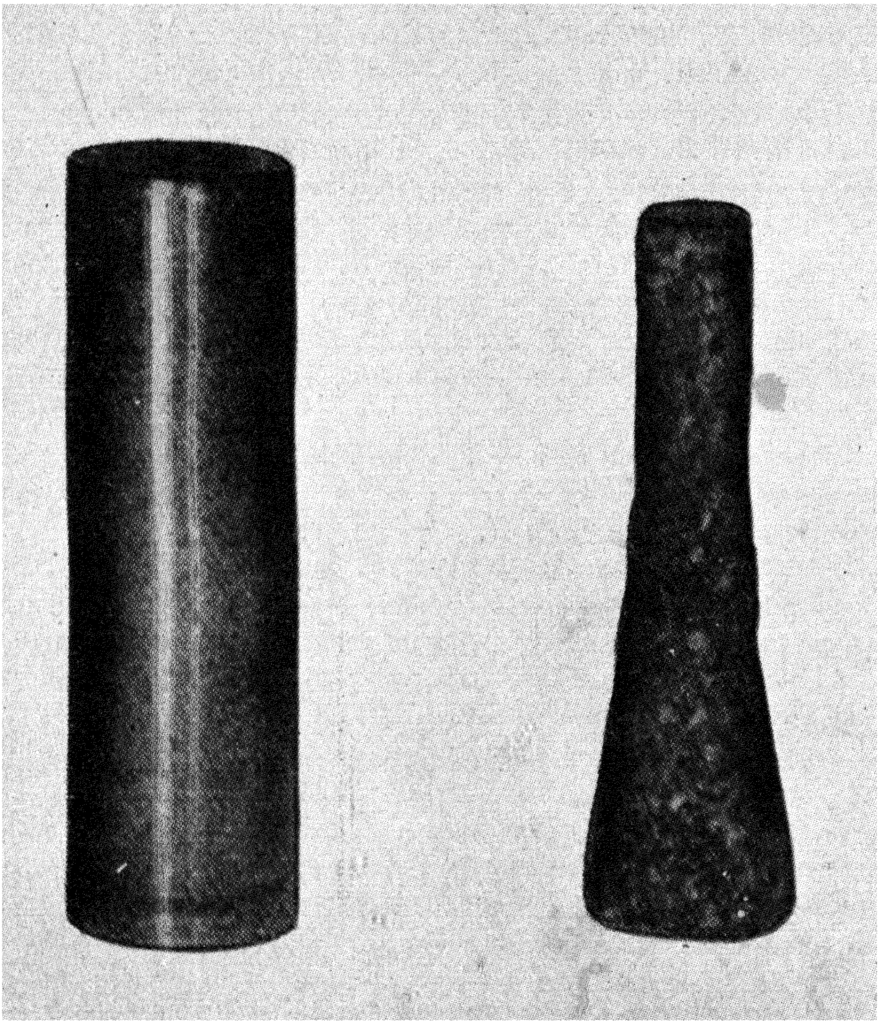
NICKEL-IRON ALLOYS ✓

The range of nickel-iron alloys containing 10–15% of nickel, with 1–3% of chromium and the same amount of copper, will be generally austenitic in character, with no graphite flakes to give a foothold for air-steam attack. As a result, they have been used as a reasonably cheap form of heat-resisting alloy in furnace work, under a variety of proprietary names, such as "Hypocrode", "Hercia", or "Iamzite". The links on a chain grate stoker can be made with such material, which is heat-treated after casting to give a machineable metal, or chilled to a martensitic form if the carbon content is suitable.

Nickel-iron alloys with little or no chromium but certain other additions have been developed to give high resistance to caustic alkali attack and generally enhanced resistance to corrosion. The "Ni-resist" group contain 6–7% of copper, with at least 14% of nickel and 1–2% of Cr and Si. They are made up with sufficient carbon to give an easy casting composition, and can be regarded as a high-duty cast iron for all mechanical properties. Entirely austenitic, the alloys can be used for a wide range of solutions which are slightly too corrosive for ordinary cast iron.[21] Thus cold dilute HCl solutions, with up to 10% of free acid, will only corrode at rates of 50–100 mdd, and $NaOH$ solution can be concentrated under ordinary pressures up to 75% solid before any notable attack commences. If the nickel content is increased up to 30% even molten anhydrous alkali has very little action.[19] The shells of caustic alkali evaporators can be made of this reasonably cheap casting metal, and combined with nickel tubes expanded into nickel tube plates. All strengths of sulphuric acid are resisted when cold (cf. Fig. V–11), but attack is rapidly increased as the temperature rises, while aeration of the cold acid also increases corrosion. The variation of attack with acid strength follows normal rules, but it would not appear that the added cost is justified when dealing with this acid. The Ni-resist alloys have been recommended for general furnace work.✓

A combination of nickel and silicon is used in such alloys as

"Audcolloy" and "Nicro-silal", which are both more resistant to corrosion and to oxidation at high temperatures than ordinary cast iron. The latter was devised for resistance to sulphur-bearing furnace atmospheres up to temperatures of 750°, while the former has been especially recommended for pump construction in handling concentrated H_2SO_4. Foodstuffs and paints do not acquire "iron stains" when in contact with these alloys, a property shared by the "Ni-resist" group. General compositions and relevant data on



(*a*) Ni-Resist. (*b*) Grey Cast Iron.

FIG. V–11.—EFFECT OF IMMERSION IN 5% H_2SO_4 FOR 100 HRS. AT 20° C.

these alloys are set out in Table V–4, which includes certain other nickel-bearing alloys occasionally met with. The 38% Invar alloy is, of course, principally noted for its very low coefficient of thermal expansion, but it is also corrosion-resistant. Aerated sea water only attacks at rates of 10 mdd over long periods of exposure. Ferrous alloys containing up to 46% of nickel and cobalt have been developed for fusing to glass—the glass-metal seals of vacuum-jacketed instruments being typical of such material. With the growing importance of high-vacuum work, these alloys will become more important in chemical practice. In corrosive conditions it can be anticipated that they will behave in the same way as high-nickel irons such as "Ni-resist". The high proportion of nickel suggests that they might be classified as alloys of that metal rather than of iron.

Table V–4

Alloy	Composition (%)	Ult. Tens. Strength (tons/sq. in.)	Brinell No.	Max. Working Temp. (° C.)
Nicro-silal	18 Ni, 5 Si, 2–5 Cr, 1 Mn, 2 C	15–20	120	950
Ni-resist	15 Ni, 2 Si, 6 Cu, 2 Cr, 3 C	14–16	150	900
Copper-free Ni-resist	18–22 Ni, 2 Cr, 1 Mn, 2 Si 3 C	14	150	—
Invar	36–38 Ni	—	—	—
Audcolloy	12 Ni, 5 Si, 2 C	—		800
Nilo Alloys	(31 Ni, 15 Co) (47 Ni, 5 Cr)	—	—	—

REFERENCES

1. Branch, A. C., and Sweeten, J. L., *Trans. Inst. Chem. Eng.*, 1949, **27**, 139.
2. Orr, S. C., *Chem. Eng.*, 1952, **59**, March, 286.
3. B.S. [S.108] (1949).
4. Inglis, N. P., "Materials of Construction", p. 96.
5. Bowman, R., *Welding Jl.*, 1951, **30**, 167.
6. Barr, W., and Erskine, J., *Proc. Chem. Eng. Grp.*, 1949, **31**, 33.
7. B.S. 970 (1947). But see B.S. 1500 (1949).
8. Tongue, H., "Manual of Chemical Engineering", Chapman and Hall, 1940, p. 120.
9. But see Monypenny, J. H., "Stainless Iron and Steel", Chapman and Hall, 1931.
10. Vernon, W. H., *et al*, *J. Iron Steel Inst.*, 1944, **150**, 81.
11. McWilliam, J. A., "Materials of Construction", p. 139.

12. Anon., *Chem. Proc. Eng.*, 1952, **33**, 247.
13. Anon., *Chem. Eng.*; 1951, **58**, Oct., 263.
14. Uhlig, H. H., "Corrosion Handbook", John Wiley and Sons, 1948.
15. Rabald, E., "Corrosion Guide", Elsevier Co., 1951.
16. B.S. 106 (1949) (3% Cr-Mo Steel).
17. Colbeck, E. W., and Mills, C. V., "Materials of Construction", p. 105. (See also B.S. 1500.)
18. Inglis, N. P., and Andrews, W., *J. Iron Steel Inst.*, 1933, **128**, 383.
19. Teeple, A. O., *Chem. Eng.*, 1951, **58**, Dec., 286.
20. Rotherham, L., *Proc. Chem. Eng. Grp.*, 1947, **29**, 46.
21. Everest, A. B., *ibid.*, 1937, **19**, 70.
22. B.S. 1501–8 (1950), 1607, 1630–32 (1950), 1750 (1051); see also *Trans. Inst. Chem. Eng.*, 1952, **30**, 152 *et seq.*
23. Hutcheson, A. M., *Trans. Inst. Chem. Eng.*, 1952, **30**, 176.
24. Forrest, H. O., *et al.*, *Ind. Eng. Chem.*, 1930, **22**, 1197.
25. *Chem. Eng.*, 1953, **60**, April (290), May (300), June (302), July (262), Aug. (260).
26. Berwick, I. D., and Evans, U. R., *J. Appl. Chem.*, 1952, **2**, 576.
27. Smith, E., *Chem. and Ind.*, 1953, Aug. Supplt., 9.

CHAPTER VI

LEAD

LEAD is the first of the "pure metal" materials, and was for many years the great standby of the chemical engineer. "When in doubt, use lead" was quoted to the author as a golden rule nearly thirty years ago by an ammonium sulphate manufacturer. In those days, however, lead was not only available in good quality, but it was relatively cheap. The price curve of Fig. VI–1 shows how this situation has altered over the last few years, and there seems little doubt that the cost of lead will go on increasing as the visible supplies of lead ores are worked out. Fortunately the use of Monel metal, aluminium, and stainless steel has reduced the need for a heavy lead construction, but there are still some fields of chemical technology in which the disappearance of lead would lead to a complete revision of existing techniques.

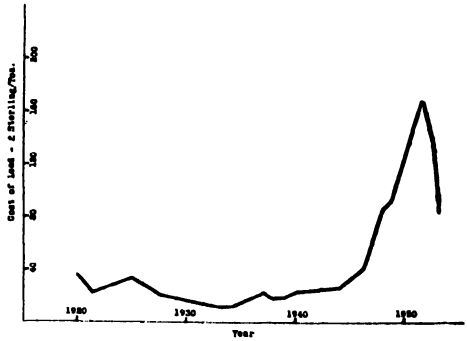


FIG. VI–1. VARIATION IN LEAD PRICES, 1920–1953.

In the form used for chemical plant, the purity of the metal is almost complete, with Pb content in excess of 99·8%. A British Specification[1] calls for 99·99%, with limits to impurities as set out in Table VI–1 below. This is Type A lead of the specification, and Type B allows for a definite addition of "protective" metals, such

TABLE VI–1

Impurity	Maximum Content %	Impurity	Maximum Content %
Copper . .	0·003	Nickel, Cobalt .	0·001
Antimony . .	0·002	Silver . .	0·002
Bismuth . .	0·005	Zinc . . .	0·002
Iron . . .	0·003		
		Lead, more than	99·99

as copper, tellurium, and silver. Any suitable composition may be agreed upon, but the limit of addition of any one metal is usually set at 0·1%, while the bismuth content is normally held at below 0·005%. The two most usual Type B leads are "tellurium" and "silver-bearing" alloys.

Tellurium Lead .	. 0·06% Cu, 0·04% Te
Silver-bearing Lead	. 0·005% Cu, 0·005% Ag

The limitations on bismuth are to some extent traditional, and an American specification[2] permits the use of metal containing up to 0·1% with 0·08% of copper. The antimony-bearing hard leads are a separate group, with corrosion resistance much inferior to chemical lead, and will be dealt with later.

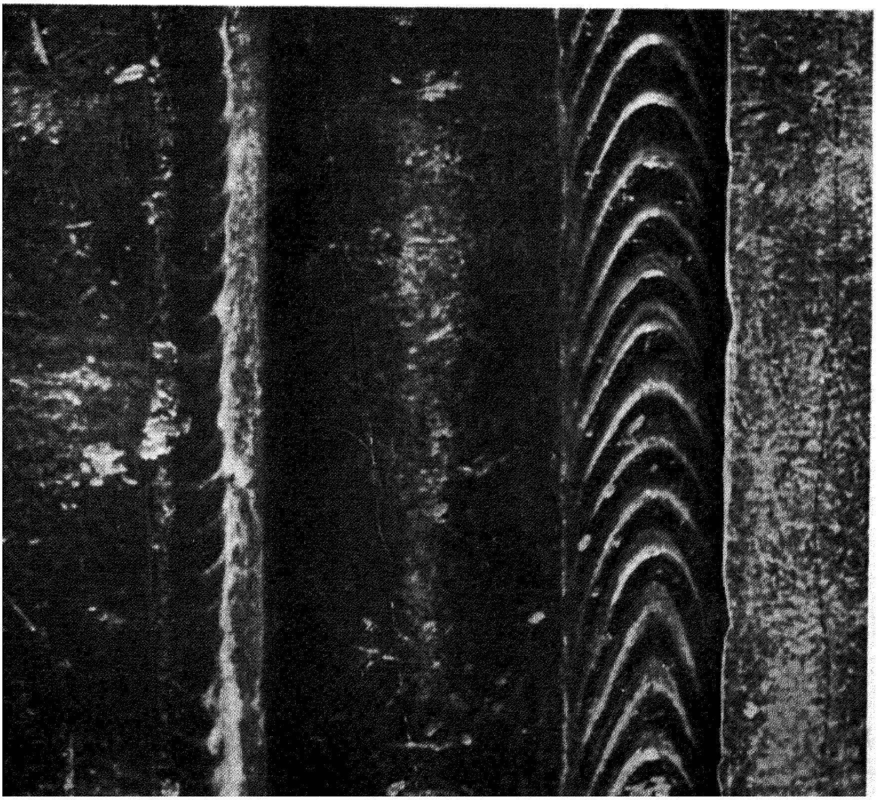
Lead is the softest and most easily worked metal used in plant construction. As a result, almost all large plant sections are built up on the site from lead sheets and pipes, while only relatively small vessels are stiff enough to stand transport. The main difficulty in design is that the metal has a very low creep stress, even at ordinary temperatures, with little or no work-hardening effects. A normal test for ultimate tensile strength, with the load applied at rates of the order of 50 lb./second, will show breakage at about 2200 lb./sq. in. with a 40% elongation (Type A lead). The same metal, under a load of 500 lb./sq. in., will give an extension of 10% in 200 days and failure, with a 41% extension, in about 450 days. The effect of copper, silver, or tellurium addition is to give some degree of work-hardening, and a consequent increase in creep stress, though there is little change in the initial strength. The mechanical failure due to creep may be accelerated by intercrystalline cracking. Lead sheet or pipe, as made, is generally of a finely grained even crystal form, but small strains tend to cause recrystallisation to a coarse, uneven structure, which is susceptible to intergranular corrosion. Again, this phenomenon is most marked with the purest leads, and an increase in the copper content to about 0·06% stabilises the original grain. Unfortunately, it is generally true that resistance to corrosion falls off, though slightly, as the percentage of impurity increases. The effective strength of a suitable lead will always be very limited, as suggested in Table VI–2. As would be expected from melting-point considerations (pure lead melts at 327°), the safe stress falls off rapidly, and it is not safe to put lead under any load at temperatures above 200°.

The metal is so soft, with a Brinell number of about 4, that it

TABLE VI–2 RECOMMENDED MAXIMUM WORKING STRESSES FOR LEAD[3]

Temperature (° C)	Type A (lb./sq. in.)	Tellurium Lead (lb./sq. in.)	Silver-bearing Lead (lb./sq. in.)
20	250	280	270
100	230	250	250
120	200	240	225
140	175	200	200
160	145	165	165

annot be machined to an accurate surface, and is quite unsuitable or any tapping or threading. All sections are assembled by homoeneous welding (lead-burning), using a pure lead wire and an oxyydrogen flame. The process is rapid, as a good worker can weld '8-lb. lead" of about $\frac{1}{8}$ in. thickness at rates up to 30 ft. of joint per our. As will be seen from Fig. VI–2, the weld metal is laid into he joint in a series of small beads, and no after-treatment is



Lead joints seen from below (left) and above (right).

FIG. VI–2.—EXAMPLES OF LEAD BURNING.

required. It has been suggested that some improvement can be made in the crystal structure at the weld by hammering, but the author has seen welds on a lead chamber wall which have resisted the action of hot nitrosyl sulphuric acid for more than ten years without any sign of local attack. These could not be hammered and were in A grade lead, which is most subject to coarse crystal formation. No flux is used in welding, and the only preparation required is a scraping of the metal surface.

The sheets to be joined in this way are graded in weights per square foot rather than in thickness. The "8-lb. lead" referred to above will thus weigh 8 lb./sq. ft., and normal grades range from 4 to 24 lb. The sheets are 6 ft. wide by 24 ft. long and can be cut to suitable dimensions with hand-shears. In building up a gas chamber or liquid container from these sheets, it is necessary to arrange for reinforcement of some kind at every two or three feet of distance. The reason for this is obvious when it is realised that the full-length sheet would be almost fully stressed by its own weight if suspended from one end. In the classic "lead chamber" process for sulphuric acid manufacture wooden beams were arranged in a lattice-work to give chequers of suitable size, and lead straps, wrapped round these beams, were welded to the sheets of the chamber. In more modern plants steel supports are used, with special clips to hold the straps, as shown in Fig. VI–3. These chambers are still the most important single type of lead chemical plant, and further details of construction are of interest.

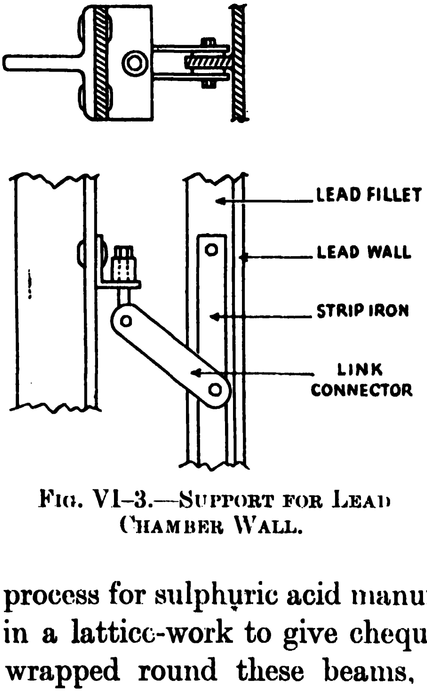


FIG. VI–3.—SUPPORT FOR LEAD CHAMBER WALL.

Until about 1920 wooden-framed chambers were widely used, and Parrish[4] describes the erection of a large rectangular unit in some detail. With the gradual change-over to smaller cylindrical packed chambers, wooden frames have been replaced by steel girder uprights and horizontal ring suspending members from pipe or angle iron. It is no longer necessary to make up the special lifting tables described by Parrish. The lead sheets are rolled to the full height of the tower, clamped at the upper end to a lifting girder, and raised by a suitable tackle to their final position. Before lifting, vertical fins 4–6 in. wide have been welded on for the full length of the sheet. These are clamped between steel flats with through bolts at 12-in. intervals, and suspending links to the framework are attached as shown in Fig. VI–3. Vertical seams between the individual sheets are made after they have hung in position for 24 hours to relax incidental strains. The suspending links are about 6 ft. apart, so that the unsupported lead "windows" are only 2 ft. by 6 ft. The top of the chamber is reinforced by concentric rings of steel flat, with lead straps at 12-in. intervals and heavy wire suspension of these rings to the overhead steel girders. Although acid practice is moving towards contact process methods and the avoidance of large lead reaction units, some chamber plants are being built, and many are still in use. Reports on German practice speak of cylindrical chambers 40 ft. in diameter and 50 ft. high.[5] The base of such chambers is normally supported on a concrete platform covered with asphalt—a necessary precaution when lead is to cover a concrete surface with free alkali present. The large-diameter pipes leading SO_2-bearing gas to the reaction units can be round or square in section, and the latter is perhaps preferable on account of ease in fixing to the supporting cradle. As all the lead is exposed on the outside, it can be patched *in situ*, generally without interfering with the process.

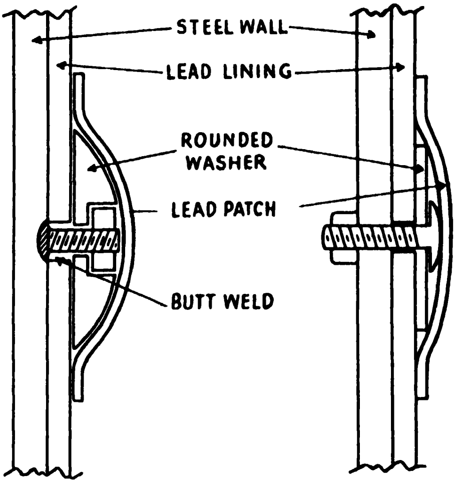


FIG. VI–4.—ATTACHMENT OF LEAD LINING.

(After Roll, *Chem. Eng.*, 1952—Jan., p. 281)

Any form of vessel can be lined with lead, building up a loose envelope from sheeting. This is attached to the outer container by some such fastening as is shown in Fig. VI–4. In these diagrams the outer sheet is steel, but the method may easily be modified to apply in wooden tanks or asphalt-covered concrete. An obvious advantage of this process is that any structurally sound but leaking tank can be given a fresh lease of life with a corrosion-resistant interior. The cost even today need not be very great when it is remembered that scrap lead fetches a very high price. The linings will spread and distort, however,[8] while they can never stand up to pressure or vacuum. If a lead lining is required for such conditions, it must be applied by the method known as "homogeneous lead lining". Steel is the normal backing metal, and must be thoroughly cleaned, normally by sandblasting, before treatment. It is then "tinned" by various proprietary solder fluxes, and sheets of lead rolled closely into this layer while the metal backing is heated locally almost to the melting-point of the cover. The lead sheets, commonly of 4–8-lb. grade, are then welded together at the edges, and a very even coating obtained. The process calls for considerable skill, but produces a lining which will not be detached by any normal operation. Pipes may be lead-lined by introducing a slightly smaller lead pipe into the steel tube, prepared as above, and putting the liner under a steam pressure of 100–150 lb./sq. in. Methods in which the lead is actually melted on to the supporting metal have been used, while copper is also used as a backing. The advantage of this combination is that the high conductivity of copper is reinforced by the chemical inertness of lead, there being no possibility of an air film between the two metals to cut down heat flow.

Lead linings are very widely used as a final impermeable membrane outside a structure built from acid-resisting brick. These bricks will always allow traces of acid to filter through, and would make working conditions intolerable. The Glover tower and Gay-Lussac tower of classical acid practice were always built with a final lead sheath. Many acid scrubbing towers may be built of steel, but to shield the steel from acid seeping through the acid-resisting brickwork a lead lining is interposed. Similarly reaction chambers can be lined with acid-resisting tile, but this is bedded down on a lead lining. As lead increases in price, substitutes such as acid-resisting asphalt, or more recently polythene sheet, become more popular. When used for this purpose, the metal is preferably screened from direct contact with the hard ceramic shapes by a layer of asbestos sheeting. This may also have the effect of partial insulation from hot acid, a very important factor in severe operating conditions. Acid concentration plants, such as the older Kessler and the newer Drum concentrator, rely on the ultimate resistance of lead to prevent acid drip or corrosion, but the hot concentrated sulphuric acid is separated from the lead lining by several inches of acid-resisting brickwork. The outer case is not lagged, but allowed to lose heat freely to the atmosphere, and never reaches a dangerous level of temperature.

Lead piping is very easy to make, and even easier to fabricate into coils for heating and cooling. Unfortunately, even liquid swirl in a stirred reaction vessel will distort these coils into the most irregular forms unless they are very carefully supported, preferably by lead-covered steel supports. Homogeneously covered metal pipes in both steel and copper can be obtained, but are not so easily built up as the ordinary lead pipe, and generally much higher in price. It may be possible to take advantage of the higher conductivity given by lead-sheathed copper. Lead has a thermal conductivity which does not vary much with temperature, and can be taken as 20 B.Th.U./sq. ft., etc., for all practical working temperatures. A $\frac{1}{4}$-in. lead wall would thus give 960 B.Th.U./sq. ft., hr., ° F., and for a 2-in. bore pipe would have a safe working pressure of about 60 lb./sq. in. A copper pipe of $\frac{1}{16}$-in. wall would be amply strong enough and could be covered by another $\frac{1}{16}$ in. of lead. Ignoring the trifling thermal resistance of the copper, the thermal conductivity of the couple would be four times as great as the heavy lead pipe. Unfortunately, heat transfer in chemical plant is generally settled by the properties of fluid films rather than by the confining metal walls, and it is doubtful if any great improvement would, in reality, be noticed. Higher working temperatures under pressure will, however, be possible. Steam at pressures above 50 lb./sq. in. should not be confined in lead pipes, while a lead-sheathed copper coil can be used with steam at 150 lb. pressure.

An interesting example of the ease with which lead can be handled is found in special concentric-pipe heat-exchangers for solutions of sulphur dioxide in an organic amine. The inner pipe is made up with a wall of six-pointed star section, the star points touching the outer tube inner surface. Concentricity is thus retained when the inner tube is in position and the pair bent to coil form. Coils of 11 ft. diameter with 2-in. bore outer tube pipes have been made and operated successfully.[6]

The cost of lead sheet in July 1952 was £161 per ton, with an additional charge of £5 for tellurium lead. Pipes were £2 per ton dearer. The metal is so easily worked that construction costs are relatively low, and should not add more than a shilling per pound to the metal charges. As mentioned above, lead is becoming one of the scarcer metals and the price will probably tend to increase in future years, despite the fact that a sharp fall in the later half of 1952 reduced the price to below £100 per ton. Depreciation costs are lowered by the value of scrap, which may be up to 75% of the initial metal price.

TESTING OF LEAD

As mentioned above, any mechanical tests on lead will give varying results owing to the very low creep stress. There is one characteristic corrosion test which is always applied, based on the rapid increase in reactivity shown by the metal as it nears its melting-point. If a small piece of lead is heated in a test-tube (with considerable caution) together with enough 96% sulphuric acid to cover it, there is very little action until temperatures of the order of 300° C. are reached. Then quite suddenly the lead disappears, often with a sharp click, and a mass of lead sulphate is formed. This is the "flash test" for lead, and all good Type A lead should show a flash-test temperature of over 300°. A Type B lead with tellurium or silver has generally a slightly lower flash test, though the temperature should still exceed 285°. Methods for the carrying out of the test are laid down in Specifications,[1] while a further measurement of corrosion by aqua regia is applied for the purest leads.

CORROSION RESISTANCE

The reaction of metallic lead with aqueous aerated solutions can be formulated as

$$\text{Anodic: Lead metal} \rightarrow Pb^{++} + 2e$$
$$\text{Cathodic: } O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

In neutral or nearly neutral solutions the anodic reaction is followed by immediate precipitation of $Pb(OH)_2$ as a firm impermeable coating over the anodic areas. Thus, although the lead concentration in the solution may be very low, further solution of the metal is completely checked. Lead pipes are often found in historic buildings which have been carrying natural waters of *p*H 5 to 9 for hundreds of years. This anodic inhibition reinforces the low solution potential of lead (—0·126 v.) to give a general inertness to all except the most corrosive solutions and some special reagents which form a soluble lead compound. These can be either acid or alkaline, and will convert the hydroxide to the characteristic salt. Reaction may then be governed by the cathode conditions. It has been emphasised that this normally involves oxygen absorption, as lead is not sufficiently electro-positive to liberate hydrogen at any measurable rate. Cathodic depolarisers can take over the role of oxygen, but may also react with lead in solution to give one of the many insoluble lead compounds. In the circumstances, it is not surprising that lead is so generally resistant to corrosion.

Sulphuric Acid and Related Compounds

This acid, in any strength, has practically no action on chemical lead at ordinary temperatures. Protection is in part due to chemical inertness, but the insolubility of lead sulphate in all but the most concentrated acids is probably the most important factor. Even when the temperature increases to nearly 100°, the rates of attack are still low. Lead chamber walls, with 60% H_2SO_4 running down freely at any temperature between 50° and 100°, will last for twenty years or more, but are reduced in thickness from a "6-lb." metal to about "3-lb." This is about 20 mdd, and illustrates another useful property of lead—the general evenness of attack. The pitting characteristic of iron corrosion is not met with, but on occasion lead can fail by cracking, as mentioned above.

Corrosion rates are increased when the sulphuric acid is richer in nitrous compounds—nitrous vitriol corrosion—but do not usually exceed 40 mdd. Properly supported lead should not fail by cracking under these conditions, but if too large an area is left between supports, cracks may appear, especially when the purest Type A lead has been used.

Strong *hot* sulphuric acid attacks rapidly, as is obvious from the flash test, and the metal must not be exposed to such conditions. A lead tank, with the metal exposed to the air, is an ideal backing for acid-resisting brickwork, as pointed out above, but should never be in direct contact with acid of more than 80% strength at temperatures above 150°. Even at lower temperatures, the soft metal is rapidly eroded by acid in movement, and lead pipes should be kept under close observation when used at any temperature above 100°. Fortunately, cast-iron or steel pipes are available for acid of above 70–80% strength, and are always used. Oleum attacks lead but there is little point in bringing the two together except in some emergency. Perhaps when chamber acid is being combined with oleum to give a monohydrate some portions of the mixing device might be made from lead, but the oleum and 100% acid will be handled in steel. The lids of strong acid containers where condensate drip can accumulate are conveniently made up in lead or lead-covered steel.

Consideration of the lead chamber process shows that the metal is unaffected by mixtures of sulphuric and sulphurous acids, but it is also unattacked by SO_2 and sulphurous acid alone. Washers for the wet gas, pumps and pipe-lines for gas or solutions, and the Cottrell precipitators are all made up in lead on every normal sulphuric acid plant. Rates of attack are extremely small, as can be seen from usage in another industry, that of paper manufacture. Here sulphite digestors for wood pulp, designed to operate at 150° with a solution containing 3–5% of free SO_2, are made from homogeneously lead-lined steel and stand internal pressures of 150 lb./sq. in. There is no evidence of cracking, and a normal lined vessel will last up to ten years or longer without lead penetration. Sodium sulphite is inert, and lead-lined vessels were generally used for the washing and sulphite purification of acid T.N.T. Lead construction was not, however, so satisfactory as that by stainless steel, which replaced lead in many factories in the later stages of the last war. The operating temperature (100°) and the rapid stirring required both tended to cause failure at any weak points, normally by cracking. Sulphuretted hydrogen, wet or dry, gives an immediate deposit of lead sulphide, and has very little further action. The removal of arsenic from 60% to 70% sulphuric acid by precipitation as sulphide was carried out in lead vessels, with lead ducting for the gases and lead-covered fans.

Nitric and Nitration Acids

Nitric acid, in any concentration, attacks lead steadily. The reaction is not vigorous, by normal standards. but corrosion rates are too fast for modern plant practice. Some thirty years ago, the only metal which would resist 60% HNO_3 (*ex* saltpetre) well enough for storage purposes was chemical lead, but aluminium and stainless steel have completely displaced it for the purer nitric acids of today. Mixtures of nitric and sulphuric—nitration acids—are not so active, and can be used in lead nitrators with almost any proportion of H_2SO_4, HNO_3, and H_2O. In particular, when the water content rises above 30%, lead is generally preferred to cast iron, and is almost as good as stainless steel. The manufacture of nitro-glycerine by the older batch process was carried out almost entirely in lead. The nitrator shown in Fig. VI–5 is an illustration of the ease with which lead can be built into complex forms with no crevices to trap the extremely unstable nitro-body. The metal is very inert towards the chemicals, and at the same time is not likely to form "hot spots" through local frictional resistance, a property always to be borne in mind when any slight abnormality may "trigger off" a detonation. When dealing with nitro-bodies after manufacture it is often necessary to heat with steam, or to inject live steam into the mixture. This will tend to distort coils, or to cut a hole through lead linings.

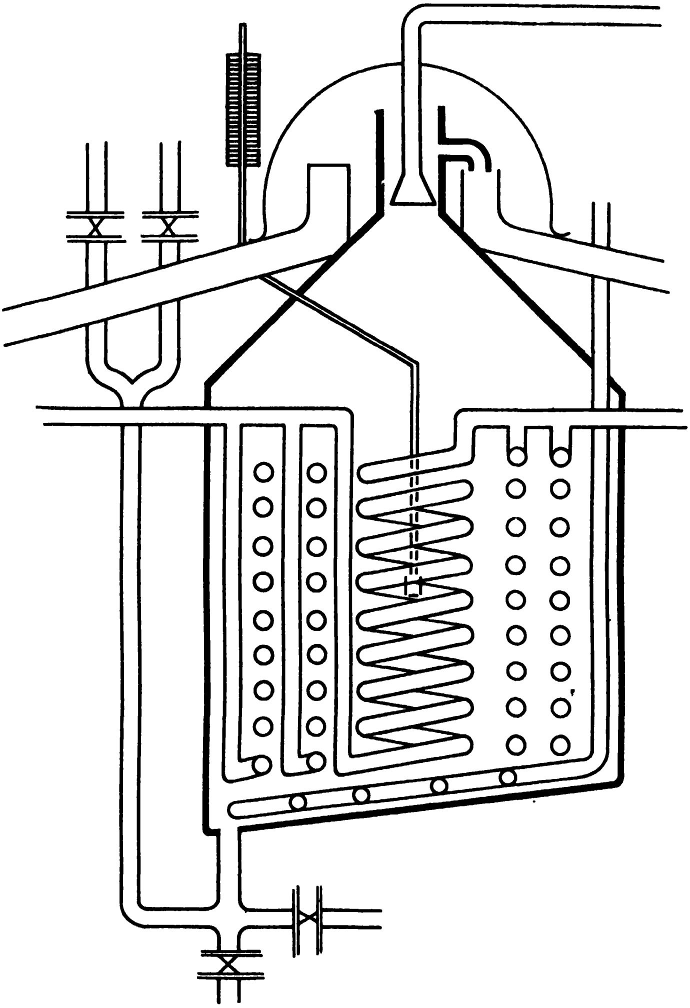


Fig. VI–5.—Heavy Lead Construction—Glycerine Nitrator.

Steam pressures must be kept down, while any steam jet should be provided with an impact plate made from acid-resisting tile. Diazotisations are generally carried out in lead plant. Iron in any form would catalyse decomposition, while wood is attacked by the free nitrous acid.

Phosphoric Acid

Phosphoric acid made by the "wet process", in which phosphate rock is treated with sulphuric acid, is quite inert towards lead in any concentration unless the temperature exceeds 150°. This may be due to the presence of calcium sulphates and fluorides, which form an insoluble salt on the metal surface, but whatever the cause, the corrosion is almost undetectable, and lead plant has been quite unscathed after ten years of continuous service. The purer H_3PO_4 made directly from phosphorus, or from P_2O_5 liberated by a furnace reaction ("dry process"), is much more active, and a hot 50% solution can give rates of attack as high as 500 mdd. This may have been in oxidising surroundings, however, and in closed vessels lead has given satisfactory service. A saturator for the manufacture of ammonium phosphate from ammonia gas and phosphoric acid, made up in lead-lined steel, was found to be quite satisfactory.

Halogen Acids

Hydrochloric acid is another chemical which was frequently handled in lead thirty to forty years ago. It can be stored cold in lead tanks and even pumped by hard-lead pumps, but no one would advocate this course with rubber-lined tanks available. Lead chloride is freely soluble in hot aqueous solutions, so that attack on the metal increases rapidly with temperature, especially when air or oxidising agents are present. Lead steam-coils, with a high depreciation rate, have been used for boiling hydrochloric acid, but once again would not be recommended when Karbate or similar materials are available. Lead fluoride is almost insoluble in dilute HF solution, and, in accordance with this, plant for manufacture and storage can be in lead, with better thermal resistance than the majority of polymer-lined plant. When the HF concentration reaches about 40% steel is preferable. Lead bromide and iodide are more soluble than the other halogen salts, and in consequence the corresponding acids are not normally handled.

The characteristic inertness is turned to good effect in organic chlorination, where the presence of iron might catalyse substitution in an undesirable position. Neither chlorine gas nor the hydrochloric acid normally liberated has any appreciable action on lead, which in consequence is the material most frequently specified for chlorinators. Iodine and bromine are more corrosive, especially the former, but it is just possible to work with bromine and HBr in the cold.

Chromic Acid

Chromic acid and acid solutions of chromate have the very corrosive effects of a cathode depolariser, but fortunately lead chromate is extremely insoluble and inhibits anodic action. As a result, this acid and its salts are normally prepared in lead, while reactions involving chromates also utilise the metal freely. It is particularly suitable for organic oxidations, as the inertness avoids any interference with reaction. Chromic acid baths, as used in plating, can be constructed in lead, though acid-resisting brickwork is perhaps a safer choice.

Alkalis

Caustic alkali solutions should not be stored or handled in the metal, as the lead hydroxide coating appears to assume a much more voluminous and porous form, allowing for penetration and further attack. A lead pipe used in an emergency for 10% caustic soda solution was blocked overnight by corrosion products, and there is no reason whatever for putting in lead plant for such work. An exception must be made for circumstances in which the reactants change from strongly acid to strongly alkaline conditions over short periods. In the operation of naphtha washing, a coal-tar distillate is washed with dilute caustic soda to remove phenols, and then with gradually increasing strengths of sulphuric acid to dissolve first bases and then unsaturated hydrocarbons. For economy in working, the whole operation is carried out in a single reactor, which is generally lead-lined. A good homogeneously lead-lined tank, with a lead-covered stirrer, will last in almost continuous use for five to ten years before repairs become necessary.

Ammonia, in concentrated solution, behaves as a weak caustic alkali, but the effects are not serious. The manufacture of ammonium sulphate is invariably carried out in lead plant, and affords another example of the cathodic resistance of the metal. Ammonia gas is blown into boiling saturated solution of the salt, while at the same time a stream of sulphuric acid keeps the acidity to about 2–4% H_2SO_4. As the ammonia is often derived from gas-works liquor, it carries into the reactor (Fig. VI–6) considerable quantities of CO_2, HCN, H_2S and other corrosive gases. A carelessly handled reactor will often go over to the alkaline side, while the acidity equally can increase to 8%. All the time violent agitation is throwing crystals of ammonium sulphate against the lead walls. Despite this very rough treatment, many saturators will last for three to four years without repair, while timely patching can keep the unit in operation for twenty years or more. When ammonium sulphate is made direct from anhydrite and ammonium carbonate, it is necessary to use lead-lined boilers for boiling off carbon dioxide from feebly acid solutions.

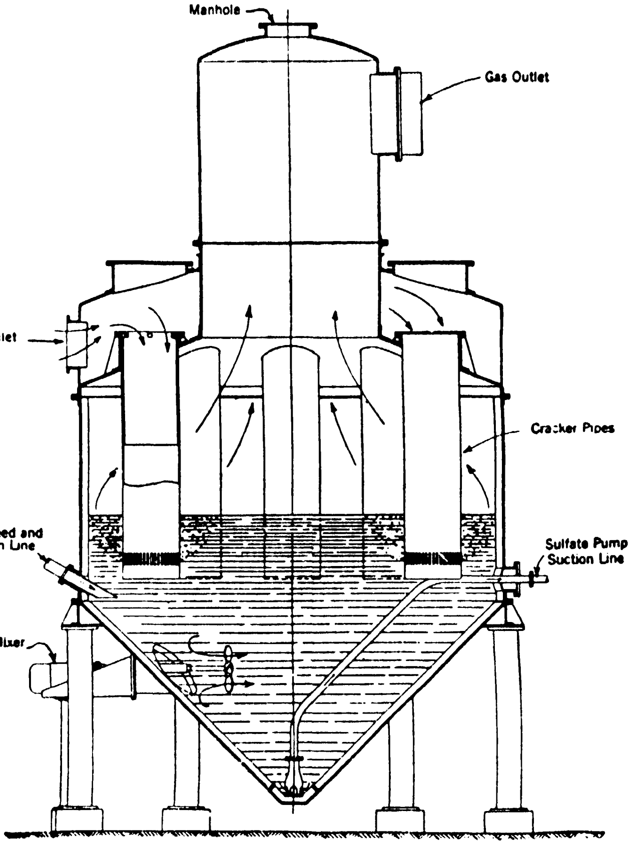


Fig. VI–6.—Lead-lined Ammonium Sulphate Crystalliser.

Continuous exposure to alkaline conditions is generally undesirable and unnecessary. Portland cement concrete has sufficient free lime to cause rapid corrosion, and cement tanks should never be lined direct with lead sheet. A preliminary lining of asphalt will be quite adequate and comparatively cheap. When lead pipes are laid underground they should never be laid in concrete, as with iron mains, and they should preferably not be laid in wood-lined troughs, which may evolve traces of acetic acid. Almost all soils contain sufficient carbonate or silicate ions to give a protective covering, and the action of sulphate bacteria may even create a stable sulphide coat. Lead water-pipes of Roman manufacture have been excavated after laying in the ground for over 1600 years, but sometimes a more corrosive soil is found.

Organic Acids

Failure of lead pipes has often been traced to the action of traces of organic acid leached from the wood of wood-lined troughs, combined with oxidation. Organic acids can attack rapidly under oxidising conditions, as indicated by the simple process for white-lead manufacture by exposure to acetic acid and air. When air is absent, the rate of corrosion is controlled by cathodic polarisation, but many organic lead salts are soluble and no other check exists. In the circumstances, lead is best avoided for strong solutions of these acids, though specific instances of use have been cited in literature.

Neutral Salts

Neutral or feebly acid salt solutions can usually be handled in lead plant, with the exception of those few heavy metals which may form lead alloys by substitution. The alums and sulphates generally have little action, as shown by considering the bulk preparation of aluminium sulphate. This is manufactured by dissolving Al_2O_3 in hot dilute sulphuric acid solution, boiling off any superfluous water, and running the hot liquid mass to open trays where it solidifies and is later broken up, or to a flaking machine. The temperature of the boiling solution can reach 160°, and there is always an appreciable amount of free acid. The operation is carried out in lead-lined boilers, with lead coils for heating. The crystallising troughs could be of lead, but they meet with fairly rough treatment in breaking up the solid mass, and are therefore made from acid-resisting brick. The behaviour of lead in the reactors is of great interest. If chemical lead is used, corrosion rates, measured as milligrams/sq. dm./day, are small, but the metal fails by cracking, as shown in Fig. VI–7. Tellurium lead, on the other hand, does not crack, but it wastes away at rates of the order of 200 mdd. This illustrates the general rule for lead corrosion that increased purity cuts down general attack but may give rise to "stress-corrosion" phenomena.

Atmospheric Corrosion

The resistance of lead sheathing to all atmospheric effects is almost complete. Many medieval lead roofs bear witness to this, and have generally proved more durable than the buildings below. The sulphur-bearing waste gas of modern industry will not stimulate attack in the same way that it does with iron, copper, or stonework, while marine atmospheres are also relatively innocuous. Iron nails are electro-negative to the metal, but are not so rapidly attacked as they would be if used with copper. Principal drawbacks to the use of lead for roofing are (*a*) the weight and (*b*) the cost. This latter is the more notable today in view of the actual thefts of lead roofing which are frequently reported (1952), and clearly use in this way is only of historic interest.

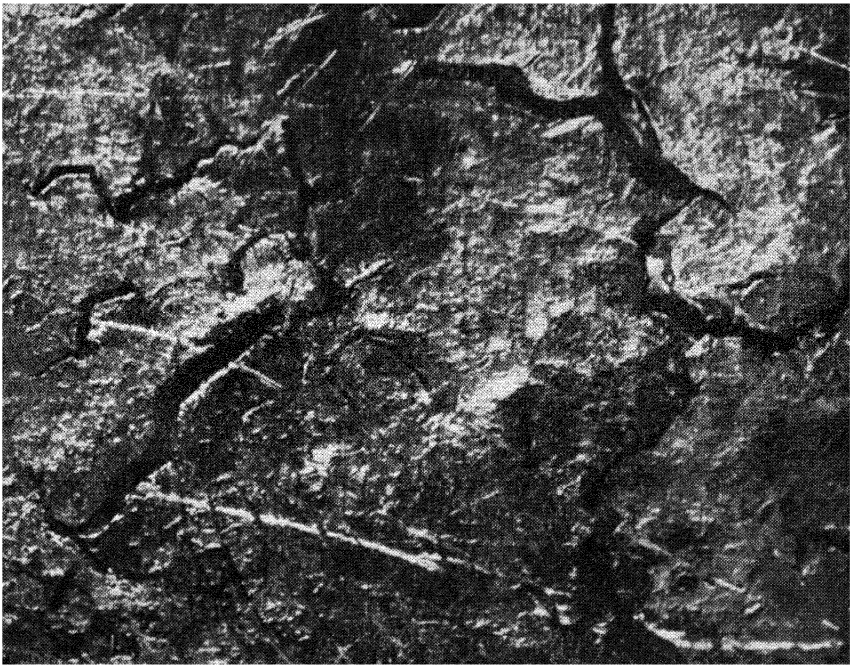


FIG. VI–7.—CORROSION CRACKING OF LEAD.

HARD LEAD

This is a lead-antimony alloy, sometimes known as "Regulus metal", and contains from 6% to 15% of antimony. As the name implies, Brinell hardness has been increased from 4 to 5, characteristic of chemical lead, to as much as 20 with the hardest mixtures. The alloys have a low melting-point, in the region of 250°, and in consequence can be very easily cast. The ultimate tensile strength increases steadily with Sb content, but so does the brittleness, while chemical resistance is also unfavourably affected. As a result, it is rare to find any but the 6–8 and 8–10 alloys in service on chemical plant. Strength and hardness, as called for by Specification,[7] are set out in Table VI–3 below.

TABLE VI–3

Antimony Content (%)	Ultimate Tensile Strength (lb./sq. in.)	Brinell Hardness No.
6–8	6000	15
8–10	7000	16
10–12	8000	17
Over 12	9000	19

Amounts of other impurity are generally below 0·2% in all, but the metal is only preferred to chemical lead because of its improved mechanical properties. A bending test is sometimes specified for the lower alloys, which are used for pipes and large plant sections. Only the 10–12% range are hard enough to take a proper screw-thread, but all can be machined to a reasonably true surface finish, and thus built up into pump or valve parts. Severe limitations are set by the low melting-points, which fixes the maximum working temperature at about 140° C., and makes it necessary to reduce the value for the safe load at ordinary temperatures (Fig. VI–8).

It is possible that the most important use for Regulus metal is in the manufacture of taps and valves for acid lines. Almost any closing device on these lines is bound to stick sooner or later, and a fair amount of force must be used to break the cementing corrosion products. If the taps are in earthenware, then the risk of breakage is very marked, while really strong alloys are expensive or more easily corroded. Regulus metal offers a reasonable compromise, even if both barrel and casing of the valve are made in the same alloy (Fig. VI–9). It is better to make the plug or barrel in high-silicon iron (Chapter X) and the casing from hard lead to avoid the common fault of two like metals "running together". Centrifugal pumps can be constructed in hard lead throughout, with the 6–8 alloy used for impeller, and mounted on a lead-covered shaft. The metal is quite stiff enough to stand up to the stresses involved in this and similar plant, while lacking the brittleness and uncertain casting qualities of high-silicon iron.

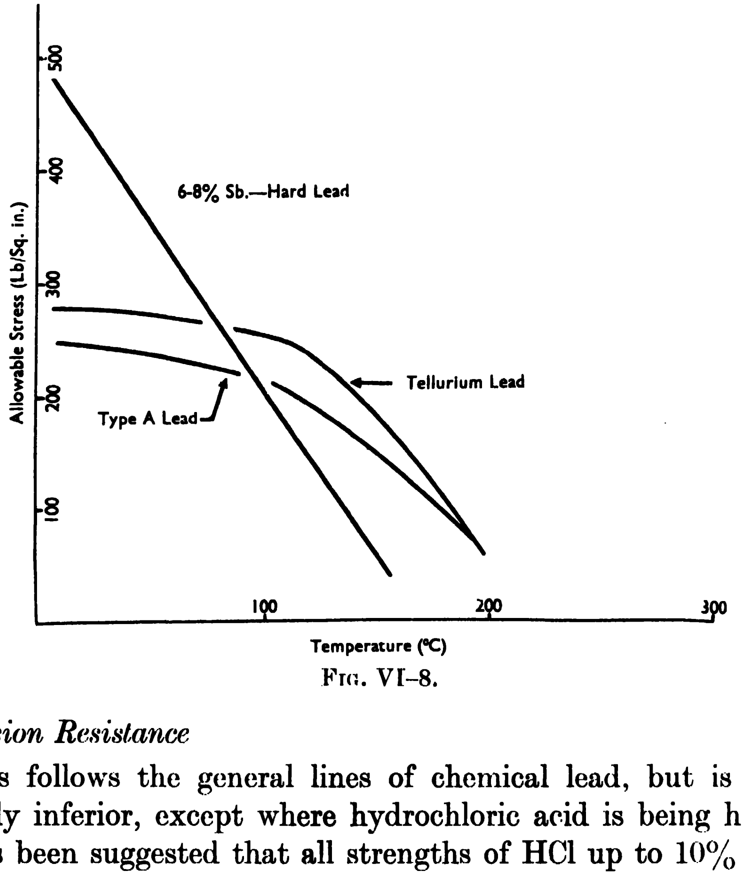


FIG. VI–8.

Corrosion Resistance

This follows the general lines of chemical lead, but is always slightly inferior, except where hydrochloric acid is being handled. It has been suggested that all strengths of HCl up to 10% can be handled in hard lead, even when hot, with corrosion rates never exceeding 100 mdd, but the matter is debatable. Certainly sulphuric acid attacks Regulus metal more rapidly than it does the purer chemical lead, but there is no marked electrochemical difference, and a hard-lead valve on soft-lead pipe does not waste away rapidly. Filter plates and frames in hard lead are much easier to manufacture than units in lead-covered steel, and have been used, with Vinyon (Chapter XIX) filter cloths, in the separation of chromium trioxide from strongly acid solution. Hard-lead pipes have been expanded into tube plates for evaporator practice, but would now be replaced, in all probability, by lead-covered copper. It is easy to join hard and soft lead together by the normal processes of lead-burning, but flanged joints between pipe and valve, or pipe and pump, are more usual.

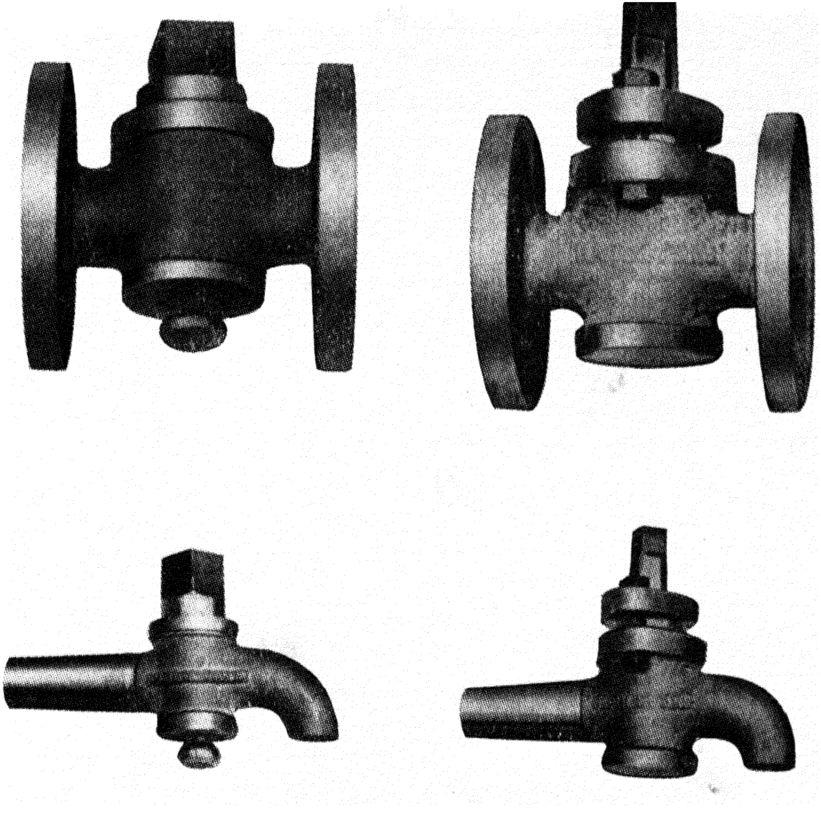


FIG. VI–9.—TAPS IN HARD LEAD AND SILICON IRON.
(Courtesy of Haughton's Metallic Co.)

MISCELLANEOUS LEAD ALLOYS

The most usual lead alloy met with in general constructional practice is the lead–tin mixture used in soft-soldering. This contains about 1 part of lead to 2 parts of tin, melts at 180°-185°, and should *never* be used permanently in any chemical plant, even where corrosive conditions are almost absent. The soldered joint is only mechanically reliable between 0° and 88° C., and the metal is more easily corroded than either of its constituents. It follows that the only advantage of the joint lies in ease and cheapness of completion, and chemical plant is seldom or never mass-produced. The action of solder is perhaps of most interest in connection with tinplate, and it will be discussed more fully under that heading.

A very common type of protection for steel sheet is hot-dipping in an alloy of lead and tin—"Terne-plate". For this mixtures containing from 5% to 25% of tin are used, and can be considered as a cheap but somewhat inferior substitute for tinplate. The low melting-point makes it possible to dip copper articles, and again the method may have advantages in mass production. Further reference will be made to the corrosion resistance in Chapter XII.

REFERENCES

1. B.S. 334 (1934).
2. A.S.T.M. B.29/43.
3. Lloyd, A., "Materials of Construction", p. 163.
4. Parrish, P., "Sulphuric Acid Reaction Chambers", Ernest Benn, 1925.
5. B.I.O.S. Rept. 1641.
6. *Chem. Eng.*, 1951, **58**, Nov., p. 161.
7. B.S. 335 (1928).
8. See, e.g., Hopkins, E. S., *Chem. Eng.*, 1948, **55**, (Mar.) 102.

CHAPTER VII

ALUMINIUM AND MAGNESIUM

ALUMINIUM—PHYSICAL PROPERTIES

THE use of aluminium and its alloys in the various engineering fields is now so widespread that an immense range of complex metal mixtures has been developed. Characteristic properties are detailed in a number of specifications,[1] but only a few are suitable for the fabrication of chemical plant. Until quite recently it was accepted practice to specify unalloyed sheet, with aluminium content of more than 99%, as the basic material, and to increase the purity figure up to a level of 99·99% as demands for corrosion resistance increased. It is now recognised that small quantities of magnesium, and to a lesser extent of manganese, can be incorporated without disastrous effects on corrosion resistance, and with a great improvement in mechanical strength.

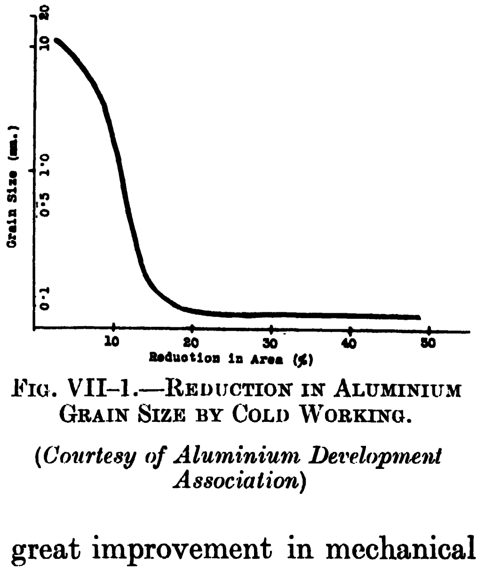


FIG. VII–1.—REDUCTION IN ALUMINIUM GRAIN SIZE BY COLD WORKING.

(*Courtesy of Aluminium Development Association*)

"Pure" aluminium, in its various commercial grades,[2] as set out in Table VII–1, is available in the hard or soft form. The metal can be softened by heating to 450°–500°, and work-hardens rapidly from this softened annealed form. Some of the alloys will actually harden at room temperatures without any mechanical work being done on the metal. During the hardening process the Brinell number changes from 20 to 50, while the strength goes up from 4 to 9 tons/sq. in. These changes are due to alteration in grain size, which follows the curve set out in Fig. VII–1. It follows from this that ideally all welds in the pure metal should be hammered to a considerable reduction in thickness for a really fine grain structure. Pure aluminium melts at 660°, and the safe stress will therefore diminish rapidly as the temperature increases above 200°. This disability will, of course, be shared by the various alloys, as suggested in Fig. VII–2.

Almost all the commercial alloys of aluminium form a two-phase solid structure on cooling, owing to the sparing solubility of other metals. Magnesium will precipitate as a complex when the content exceeds about 3%, and copper has a final solubility at ordinary temperatures of less than 0·2%. Precipitation of these alloyed metals as complex crystals leads to the formation of an irregular surface, while the all-important oxide film (see below) may not form. Duralumin alloys containing copper are particularly prone to corrosion, and though mechanically the soundest of these light alloys,

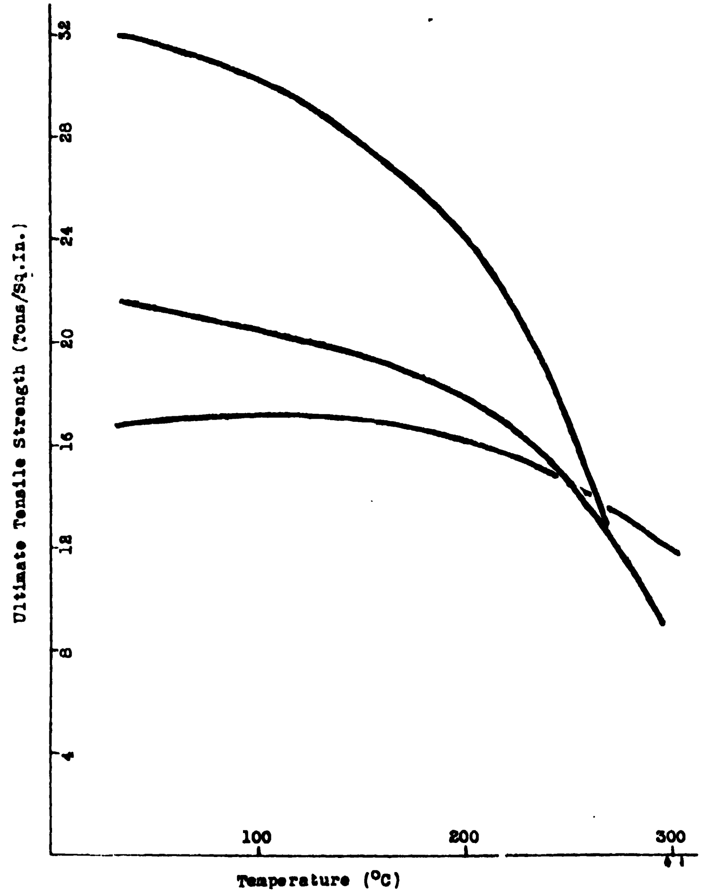


Fig. VII–2.—Temperature-strength Curves for Aluminium Alloys.

they are never used alone in corrosive conditions. The magnesium-bearing metals represent the best compromise between corrosion resistance and strength, while manganese, in small quantities, has something of the same effect. Castings in the pure metal are unsound, and the usual casting alloy contains 10% of silicon. For chemical plant this can be replaced with advantage by a magnesium casting alloy, details of which are set out in Table VII–1 below.

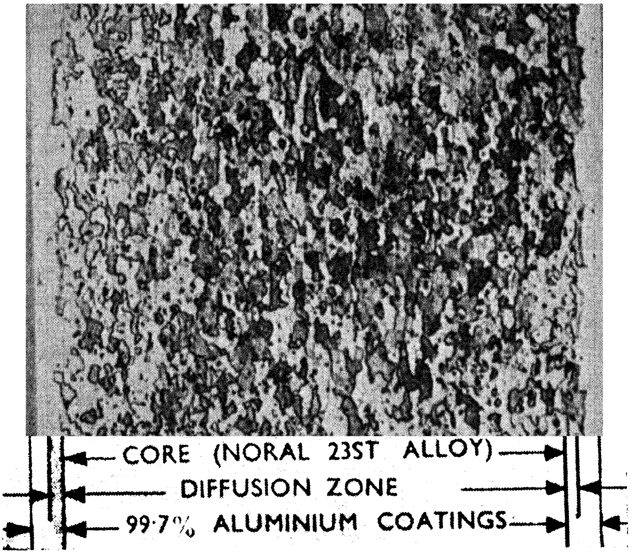


Fig. VII–3.—"Clad" Aluminium Composite Plate.

(*Courtesy of Messrs. Northern Aluminium Co.*)

It is possible to combine the best properties of pure aluminium with the strength of duralumin by using the clad-sheet principal. A hot-rolling process is used to give an envelope of 99·5% metal on the 4% copper alloy. These sheets, known commercially as "Alclad", are extremely stable, with the inner layers completely fused to the purer coat, as shown in Fig. VII–3. Unfortunately, the fusion is so good that the alloying elements of the interior diffuse to the surface during any prolonged heat treatments, and the danger of this occurring during a welding process is obvious.

Pure aluminium has a specific gravity of 2·7 at 20°, and the alloys above range from 2·65 to 2·75 (approximately 0·1 lb./cu. in.). As the corresponding figure for alloy steels is about 7·9, the strength-weight ratio of aluminium is greatly in its favour—at any rate for atmospheric temperatures. If the safe load on a 3% magnesium alloy is taken at 3 tons/sq. in., a cylinder of 3 ft. diameter, withstanding an internal pressure of 200 lb./sq. in., will need a wall thickness of ½ in. If the cylinder is made in mild steel, and the safe load is taken at 6 tons/sq. in., then a ¼-in. wall is sufficient, but the vessel will now weigh half as much again as the aluminium alloy unit. Where stiffness and resistance to shock are concerned, rather than simple tensile strength, the advantage of aluminium alloys is still more marked, as shown by the growing use of aluminium containers, tank wagons, and even scaffolding.

The tensile strength figures shown in Table VII–1 are taken at ordinary temperatures, and it may be assumed that the strength will fall off with temperature increase in the way suggested by Fig. VII–2. The rapid fall at levels above 200° C., suggests that this should be regarded as a practical limit for all aluminium alloys under stress. Many engineering applications involve higher temperatures (e.g. engine pistons), but these are not commonly combined with corrosion. On the other hand, mechanical strength is retained down to liquid air temperatures, and the metal does not become brittle.[4]

PLANT FABRICATION

Even the purest aluminium is far more suitable than lead for direct construction, and it is quite usual for large plant to be rigid and self-supporting. The typical aluminium vessel has been built up from sheet, welded throughout, with such sections as flanges reinforced by steel rings. Riveted construction is unusual, though quite possible. Marine engineering has generally relied on riveting, using a 5% magnesium alloy for rivets, which can be driven either cold or hot (450°).[5] This may be a continuance of the shipbuilding tradition, and provides crevices for local corrosion. Fusion welding seems a much sounder proposition, and can be carried out either by gas or electric-arc processes. There are two "mass-production" methods also available—resistance and direct pressure—but these are seldom applicable in chemical plant.

The main problem in welding is to prevent oxidation and oxide inclusions; a heavy flux layer is required, specifications for which have been laid down.[6] It consists essentially of chlorides and fluorides of the alkali metals, and arrangements must be made to wash these from the joint after welding, or corrosion centres will be set up. The joints should be designed to avoid any flux inclusions, as shown in Fig. VII–4, and then scrubbed with hot water, or even dilute nitric acid. Aluminium alloys have twice the thermal expansion of steel, and welds which do not allow of after-shrinking may crack on cooling. In all gas welding, and to some extent in arc welding, there is a tendency for water to be absorbed as oxide and hydrogen. The latter is liberated from the metal in cooling to give a porous weld, so that all surfaces should be cleaned and dried before starting operations. Wherever possible the finished joint should be cold-worked by hammering, together with the surrounding areas, to give a uniform grain structure. It is generally true that annealed metal is cathodic to the hard metal structure, so that the weld metal and surrounding areas will not be preferentially attacked on this account, but the very large crystals of metal which may exist are better broken up by cold-working. The latest welding process utilises argon gas as a screen and dispenses with a flux. A tungsten metal arc is used, giving welding speeds up to 8 ft. per minute, with an argon usage of less than 20 cu. ft. per hour. The method is too

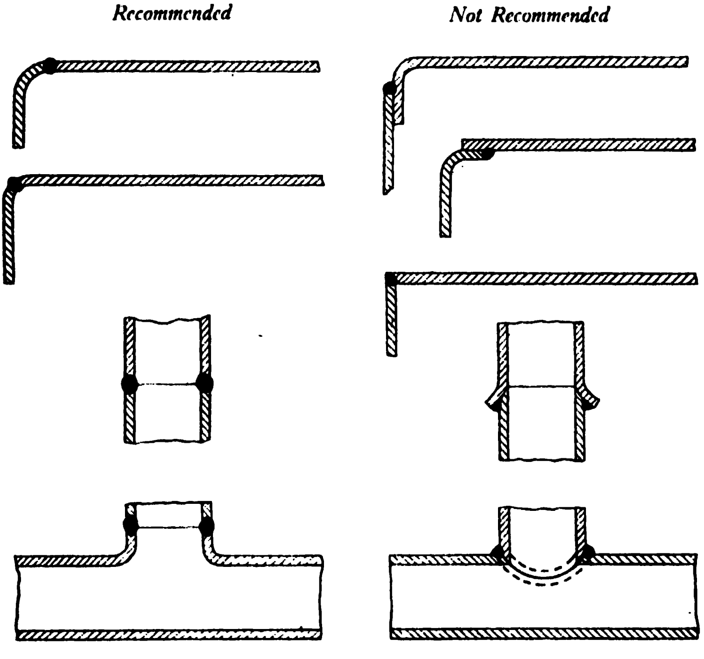


FIG. VII–4.—THE DESIGN AND POSITION OF GAS-WELDED JOINTS IN ALUMINIUM.
(*Courtesy of Aluminium Development Association*)

costly for most purposes, but appears to give a sounder weld than any other method.

Brazing, with the use of an aluminium-silicon alloy, is quite straightforward when the pure aluminium metal is used, but has not so far been employed with magnesium-bearing alloys. As the joint will almost certainly be more easily corroded than the main body of the metal, such methods will not be acceptable for chemical plant.

The Aluminium Development Association[7] have issued bulletins on the joining of aluminium parts which cover operating techniques very fully.

In plant design, it should be noted that thermal conductivities for all alloys are high and relatively unaffected by temperature. Pure aluminium has a conductivity of 133 B.Th.U./sq. ft., etc., at —50°, and this does not alter appreciably over the whole range to 400° C. The magnesium and copper alloys are appreciably lower at 80 to 95, but still retain these values as the temperature rises, while the casting silicon alloy has a value around 50. This is higher than any common metal except copper, and allows the use of thick walls in heat interchangers without loss in efficiency. Another interesting property of aluminium is the very low emissivity for radiated heat. Even rough plate has a value about 10% of black-body conditions, while the polished surfaces drop to 4%. Sheathing of a furnace wall by aluminium can reduce heat losses very considerably, as the emissivity is reduced by 90% compared with an oxidised iron surface or plain brickwork.

ALUMINIUM COSTS

There can be no conceivable shortage of aluminium ores, as the element in one form or another is abundant all over the world. The cost of the metal is almost entirely one of electric power, and it has been described as solid electricity. Despite the increase in this basic cost with general fuel shortages, the change has not been so marked in the metal price, due to improved techniques and larger plants. There has been relatively little change over the last twelve months, and the price of sheet (in July 1952) was 26 to 36 pence per pound. Tubes are a few pence more expensive. Plant fabrication is straightforward, but the welding demands more skill and care than for steel work. Manufacturing costs can therefore be estimated at 12 pence per pound for large plant, rising to 36 pence for small complicated units. Aluminium plant might therefore cost from 3*s*. to 6*s*. per pound (£360 to £720 per ton).

RESISTANCE TO CORROSION

Clean metallic aluminium is extremely reactive. Even exposure to air at ordinary temperatures is sufficient to give immediate oxidation, while boiling water reacts vigorously to give gaseous hydrogen. This reactivity, however, is self-inhibiting, in that a film of oxide a few molecules thick soon covers the metal surface so completely that no bare metal is exposed. This film, about 10^{-5} mm. in thickness, is generally a complex hydrate ($Al_2O_3 . H_2O$)[8] and is peculiar in that it is almost impermeable to the flow of electrons or ions at ordinary ranges of temperature. If any process lifts or dissolves the film the metal reacts as would be expected from its place in the electrochemical table (Chapter I). The intensity of reaction can be shown by rubbing a bead of mercury into a fresh scratch on an aluminium plate. A small pyramid of oxide can be *seen* to grow, reaching a height of several millimetres in a minute. On the other hand, extremely corrosive liquids have practically no effect on the metal when once the oxide film has formed.

Aluminium is therefore a perfect example of a metal protected by anodic inhibition. If the film breaks down at any one point, intensive pitting may be expected, while oxidising conditions should always be promoted. When the film of oxide breaks in reducing solutions, very extensive corrosion can be expected, but the very rapidity with which it forms shows that in oxidising solutions breaks in the film will heal at once. Boiling aqueous triethanolamine pitted to penetration $\frac{1}{8}$ in. thickness of metal in two hours, but boiling 96% HNO_3 gave no marked action over several years.

In view of the great importance of the surface film, it has often been thought essential to form the oxide by deliberate reaction rather than by casual aeration. The most general method is one of electrolytic oxidation, the metal forming anodes in a bath of 15% H_2SO_4 solution. A current of 10–15 amperes per sq. ft. for 10–30 minutes gives a porous deposit some 10^{-2} mm. thick, which is hardened and hydrated by 20 minutes' boiling in water. Other electrolytes such as chromic, oxalic or boric acids may be substituted for the H_2SO_4, while the subsequent sealing is enhanced by the presence of chromates, nickel or cobalt salts, and patented organic fillings. Anodically oxidised surfaces are extremely resistant to all atmospheric attack and to corrosion by sea water. They can be dyed in many attractive colours, and are generally more important for decorative work than for chemical plant. When a container is required which has no staining action on a delicate chemical, these prepared surfaces can be considered, as compared to Monel metal or stainless steel. Leather-dyeing tanks in "Birmabright" (anodically oxidised magnesium-bearing alloy) are preferable to both these when using weakly acid dye solutions. As an alternative to electrolytic anodising, a surface oxidation with chromates may be used. The "MBV" treatment is based on immersion in a bath of alkaline sodium chromate, and gives an excellent base for paint films.

The inherent reactivity of the metal may lead to unusual forms of corrosion. A vessel for hot concentrated tartaric acid solutions was unattacked from the inside, but a faintly acid cooling water caused such intensive pitting from the outside that the metal was pinholed in less than six months.[9] This particular emergency was met by cathodic protection, strips of zinc being attached to the metal at 2-ft. intervals. In acid conditions zinc is anodic to aluminium but the polarity may be reversed in alkaline solutions. Complete cathodic protection is not easy, as suggested by Table VII–2. This shows that magnesium is probably the only suitable metal for use as a sacrificial anode, and also indicates that nickel, copper, and many alloys should never be fitted in direct contact with aluminium sections of a chemical plant.

TABLE VII–2 ELECTRODE POTENTIALS AGAINST COMMERCIALLY PURE ALUMINIUM, MEASURED IN 3% NACL SOLUTION, UNAERATED, AT 22° C

Metal	Potential (mV.)	Metal	Potential (mV.)
Magnesium . . .	−820	Tinplate .	+100
Zinc Base Alloy . .	−330	Solder . .	+280
Galvanised Iron . .	−300	Brass . .	+460
Cadmium Plate . .	−20	Stainless Steels	+410 to +710
Mild Steel . . .	+60		
Cast Iron . . .	+50	Copper .	+580
Duralumin . . .	+30	Monel metal .	+600
		Nickel . .	+620

(After "Properties of Aluminium", Aluminium Development Assn.)

Now aluminium is generally too soft, even in alloyed form, to make up into valves or pump parts. When these must be made in stainless steel, or an acid-resisting bronze, and connected to aluminium pipes or tanks, it is good practice to put some form of insulator between the two metals. Ideally, this may take the form of a distance-piece made from a synthetic resin such as Keebush, but non-conducting resin or rubber washers may be inserted between flanges. A specification of the Ministry of Supply[10] covered some of these jointing materials, while a zinc chromate paint has been recommended for general use where possible. As a comment on the limitations of electrochemical theory, it has been claimed that stainless steel and aluminium can be directly connected without any untoward effect; in a quoted case,[11] aluminium pipe-lines carried hot concentrated acetic acid directly into a stainless-steel vessel with no signs of local attack.

Corrosion figures for so light a metal as aluminium tend to give a misleading picture when expressed in the normal manner of milligrams per square decimetre per day. A penetration of 0·02 in. per year is equivalent to 38 mdd, while for steel the same weight rate of attack would only mean about 0·007 in. of thickness lost per year. It must again be stressed, however, that both figures fail to represent the true state of corrosion, which is almost always irregular. Aluminium is a particular case of this kind, often failing through intergranular penetration while the bulk of the metal retains its original thickness and weight. However, it may be supposed that corrosion rates exceeding 50 mdd will probably mean that the plant cannot be operated economically—about half the rate previously suggested for iron and steel.

Sulphuric Acid

Cold dilute acid solutions have very little action on the metal, especially if an anodising treatment has been applied. Use for dye baths has already been mentioned, while the centrifugal baskets spinning artificial fibres free from acid are also made from an oxidised alloy. As the concentration of H_2SO_4 increases, rates of attack also increase, and very soon reach uneconomic levels, as shown in Fig. VII–5. Maximum rates of attack are shown with concentrations around 70%, and there is a sharp fall as the acid approaches anhydrous conditions. Aluminium is a possible alternative to steel in the handling of oleum or liquid sulphur trioxide, a somewhat surprising fact when the behaviour of anhydrous organic acids is taken into account (see below). The passivity of aluminium with sulphuric acid is soon destroyed as the temperature rises, and boiling solutions of acid of any concentration attack rapidly.

Nitric Acid

The manufacture of nitric acid from ammonia, in bulk, has been made possible by the free use of stainless steel and aluminium. At ordinary temperatures the two metals are almost interchangeable for any strength of acid. It is true that Fig. VII–6 suggests higher rates for aluminium corrosion up to about 80% HNO_3, but the results of tests are rather artificial, and either metal can be freely used. As the temperature increases rates of attack on the aluminium become more marked, but it is still to be preferred to stainless steel for any concentrations

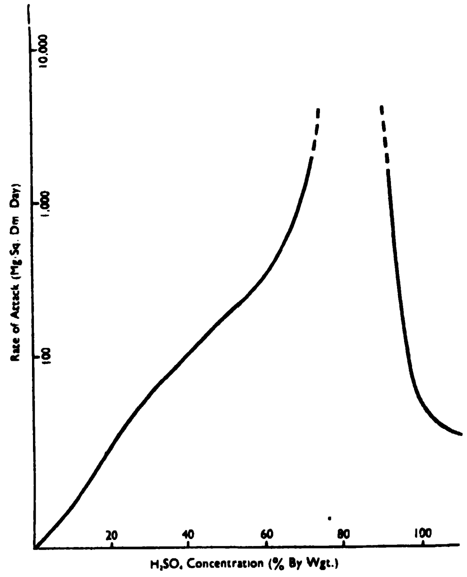


FIG. VII–5.—ACTION OF SULPHURIC ACID ON ALUMINIUM (99·9 Al).

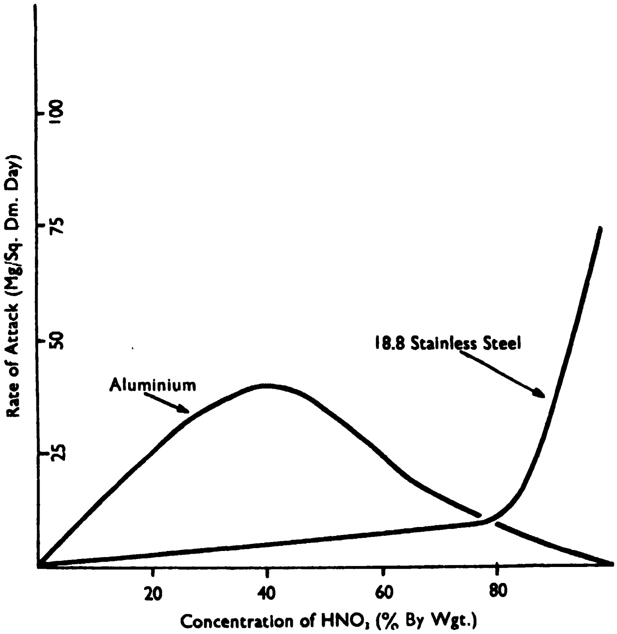


FIG. VII–6.—ATTACK OF COLD NITRIC ACID ON STAINLESS STEEL AND ALUMINIUM.

above about 90%. An annoying form of corrosion can occur when aluminium plant containing hot concentrated acid leaks slightly. The liquid picks up moisture from the air, and attacks the hot metal wall from the outside. If this can be avoided, aluminium has a very long life in extraordinarily severe conditions. The Bamag process for nitric acid manufacture demands a metal that can withstand mixtures of HNO_3 and NO_2, under pressure at 150°, with traces of water in the earlier reaction stages. Liners for the autoclave are made in ordinary aluminium of 99–99·5% Al and can have a working life of five years or more.

As compared to stainless steel, the metal is not so mechanically reliable, especially at higher ranges of temperature, but is not nearly so susceptible to "weld decay" or localised attack around the welds. Aluminium tanks and containers of all kinds have the obvious advantage of lightness. On a small scale, drums of 5 gal. capacity weigh about 3 lb., as compared to 45 lb. for a glass carboy and 23 lb. for a stone bottle (quite obsolete in this country). Rail tanks are only half the weight of steel and have the added recommendation that they need not be painted. As mentioned above, the high reflecting power of the metal surface ensures that the tanks will not heat up unduly in strong sunlight. The softness and ductility of the metal have ensured the survival of aluminium tanks without leakage in quite disastrous crashes.

Other Inorganic Acids

The metal is unsuitable for use with hydrochloric acid, whatever the strength. Apparently the chloride ion can penetrate any oxide skin, and acid conditions lead to stripping to expose the metal. A small proportion of chloride in nitric acid, as in the product from saltpetre, will set up rapid corrosion, though in the cold the action is not violent. Other halogen acids will also attack, though hydrofluoric is relatively inert. This latter, when combined with concentrated phosphoric acid, has little effect on the aluminium plant used for substituted phosphorus derivatives. Sulphurous acid and sulphur dioxide pit the metal rapidly, but sulphuretted hydrogen and sulphide solutions are extremely inert. It is quite usual to build fans and conduits for moist hydrogen sulphide from aluminium, which thus provides a useful substitute for lead. Unfortunately, this is not combined with the stability of the latter towards any oxidation products.

Organic Acids

This is the second great field of application for the metal, which combines a fair degree of resistance with the formation of colourless corrosion products. Copper and iron in any form will not be rapidly attacked by many organic acids, but they will cause discoloration. One restriction always applies in the use of aluminium and its alloys—the rapid increase in corrosion when perfectly anhydrous acids are being handled at high temperatures. Hot solutions of propionic acid, for instance, only attack at rates of the order of 10 mdd until the concentration exceeds 99·5%, but if this acid becomes anhydrous, rates may go up to 200,000 mdd, and thick metal sections may be perforated in a few minutes, as shown in Fig. VII–7. The action of anhydrous organic compounds is not confined to acids, as many hydroxyl-substituted derivatives behave in the same way. Both pure metal and magnesium-bearing alloys are attacked, but the action is more localised, and more dangerous, on the former. Thus phenols can be handled, with some corrosion, in magnesium alloy, but will penetrate the pure metal. The action is peculiar to the anhydrous compounds, and changes in a process which produce these conditions should always be observed with care.

When anhydrous attack is avoided, resistance to most acid-reacting organic compounds increases with the acid concentration. Thus a 10% acetic acid solution attacks at a rate of 400 mdd, while the 90% acid attack has dropped to 100 mdd. This is a considerably higher figure for corrosive attack than is given with copper (Chapter VIII), but the corrosion products are not coloured, nor is the corrosion greatly increased in the presence of oxygen or oxidising agents. Oxidation processes, such as the conversion of acetaldehyde to acetic acid, or methyl alcohol to formaldehyde, are commonly carried out in aluminium plant, with due care to avoid boiling anhydrous acids.

The metal is specially valuable for handling delicate chemicals which must not acquire metallic taste or colour. Lemon juice corrodes at rates up to 140 mdd, and even milk will give figures of the order of 50 mdd, but the products are not stained in any way, nor does a metallic taste develop. The salts are *said* to be non-toxic, though there is a difference of opinion on this point. Linseed oil boiled in copper or steel darkens much more rapidly than when aluminium vessels are used. It is common practice to make the bottom of the boiler in heat-resisting copper, but the top, where refluxing oil meets the oxidised metal, in aluminium. Many varnishes are mixed and boiled in aluminium plant, and water-white synthetic resins have their final stages of manufacture in aluminium reaction vessels.

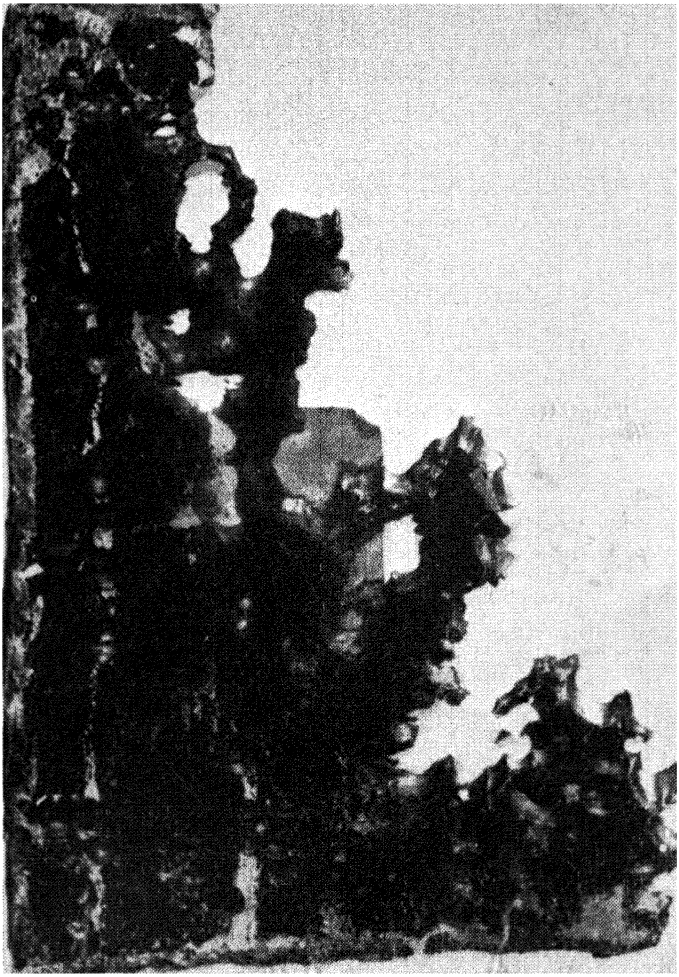


FIG. VII-7.—EFFECT OF ANHYDROUS PROPIONIC ACID ON ALUMINIUM.

Alkalies

Aluminium hydroxides are readily soluble in caustic alkali, and obviously the metal is unsuitable for this group of chemicals. It may be possible to use silicates as an inhibitor. The rate of attack of a 10% solution of sodium carbonate is about 3000–4000 mdd, but the addition of 0·2% of sodium silicate reduces this to below 10 mdd. The attack of caustic alkalies cannot be so inhibited, and a boiling 5% solution of caustic soda containing 1% of silicate still corrodes at a rate above 10,000 mdd. Ammonia solutions are less active, but the metal is not really suitable for such work. Many industrial detergents and cleaning materials contain free alkali; if used indiscriminately on aluminium plant, these will set up local centres of corrosion, and in any case tend to break down the protecting oxide film for other reagents. When the aluminium is to be cleaned, special fluids, largely developed in connection with the dairy industry, are readily available.

Neutral Salts and Aqueous Solutions

The salts of various acids generally follow the acid action. Nitrates, with the exception of those of the heavy metals, are reasonably stable towards the metal. In particular, ammonium nitrate is generally handled in aluminium or stainless steel, and the former has the advantage that traces of aluminium do not render this material unstable. Mixers for incorporating T.N.T. into ammonium nitrate have the advantage of inertness and no sparking characteristics, and many other explosive mixtures of organic nitro-bodies can be treated similarly. Sulphates may attack at boiling-point, and sulphites definitely pit the metal. Chlorides will usually set up pitting, but the improvement given by magnesium alloys over the pure metal has been noted.

Aluminium has no apparent action on micro-biological processes. The production of antibiotics by deep-vessel fermentation has become an extremely important branch of the chemical industry. The fermenting tanks can be aluminium,[12] as well as the various absorbing and extracting units. Here the really critical feature is that the plant shall have no action on the chemicals, as any diminution in biological activity would have very serious results. In general, all fermentation plant for the production of alcohols or ketones from sugars can safely be built from aluminium, unless the inorganic reactants concerned have some action on the metal.

Another important chemical on which aluminium has no action is hydrogen peroxide. Stainless steel is quite unattacked by the solution, but catalyses the decomposition to an extent which is definitely dangerous with the more concentrated solution being made today. High-purity aluminium, here to be preferred to magnesium alloys, is relatively unattacked, and does not catalyse decomposition, even at concentrations of 90% H_2O_2 and over.[13]

Organic Compounds

Neutral hydrocarbons, as would be expected, have little or no action, and the metal, but for cost, would be widely used for such plant as will not be required to stand up to temperatures above 250°–300°. Rail tanks for petroleum oils have been made in aluminium, and a recent development in which foil is interleaved with paper has allowed the use of "throw-away" oil cans in the U.S.A. The effect of anhydrous acids has already been mentioned, but the metal can also be pitted very badly by solutions of organic amines. Boiling ethanolamine in water will perforate a metal wall ⅛ in. thick in a few hours, incidentally providing an illustration of the misleading nature of weight corrosion figures.

Atmospheric Corrosion

Ordinary sheets of aluminium and of aluminium alloys will be covered by an oxide film in a few minutes at ordinary temperatures, and the thickness will not increase notably, after this initial reaction, for many years. Rapid oxidation can only be obtained by raising the temperature to about 450°–475°, and is apparently unaffected by the presence or absence of moisture. It is not necessary to paint, and the light-reflecting surface of the untreated metal is usually an asset. If painting is necessary the oxide film forms a perfect natural base, and no treatment is required. On the other hand, plating for ornament or hardening is made difficult by this very film, and no really effective way of plating aluminium with a good adherent film has yet been discovered. A process has been suggested in which wet sand-blasting prepares the metal surface and at the same time covers it with a protecting slurry layer. The plate is then lowered rapidly into the plating bath, and the onset of metal deposition washes off the slurry as a loose precipitate. This may provide a way to overcome the surface abrasion which is often annoying with moving aluminium parts.

MAGNESIUM

This is the lightest metal which can be used in plant construction, with a specific gravity of 1·74, as compared to aluminium at 2·7, and may present great attraction where small weight is essential. The rapid development of aeronautical practice has already led to the proposal that liquid-air stills be erected for aircraft to supply oxygen, while many chemical plants of the future may well be needed in almost inaccessible situations. In these circumstances magnesium and its alloys may become of importance in chemical plant work, despite the great reactivity of the metal. The standard electrode potential (—2·30 v.) is higher than any metal with the exception of the alkalies, and such a material cannot possibly be used in contact with any electrolyte unless protected by anodic oxidation. The pure metal is too soft for any practical use, and alloys containing up to 10% of aluminium are normally employed. Some zinc and manganese mixtures are also being developed, and a cerium-zirconium mixture has recently appeared.

A typical alloy with 9% of aluminium and 2% of zinc will have an ultimate tensile strength of about 10 tons/sq. in. as cast, but can be heat-treated and age-hardened to nearly twice this strength. The Brinell hardness of 60–80 is just enough for general machining, while welding is the normal method of joining.

Resistance to any form of corrosion is due to the oxide film which forms as the metal surface is exposed to air. The effectiveness of the film is very sensitive to traces of iron and other related metals. For instance a 6% aluminium alloy corrodes in aerated sodium chloride solution at a rate of 20 mdd, but if the metal contains as little as 0·01% of iron the rate of attack goes up to over 3000 mdd. Even the pure metal film is dissolved immediately by all mineral acids, with the exception of hydrofluoric and chromic, and most organic acids are equally active. Dilute alkaline solutions do not attack at ordinary temperatures, but corrosion increases steadily with temperature, and may become violent at the boiling-point. Fluorides in solution check the reaction, and undoubtedly function as additional anodic inhibitors. Even the feeble action of lead tetraethyl and related compounds in petrol mixtures can cause serious corrosion, especially if any water is present. Traces of chromate will check this latter action to some extent. It is obvious that magnesium alloys will only be used in exceptional circumstances, and plant will only handle neutral or faintly alkaline solutions, preferably containing either a fluoride or a chromate as inhibitor. A chromate-fluoride pickle has been claimed to prepare magnesium surfaces against corrosion, just as anodising prepares aluminium.[14] For structural purposes magnesium alloys will be more important in the future, as supplies of raw material are inexhaustible, and the cost relative to other metals is tending to drop.

REFERENCES

1. B.S. 1470–1490.
2. B.S. 1470, SIA, SIB, SIC.
3. "Properties of Aluminium", Aluminium Development Association, 1949.
4. Colbeck, E. W., *Trans. Inst. Chem. Eng.*, 1949, **27**, 55.
5. Venus, J., *Trans. Inst. Eng. Ship. Scotland*, 1951, **95**, 22.
6. B.S. 1126 (1943).
7. A.D.A. Bulletin No. 5, "Gas Welding"; No. 19, "Arc Welding".
8. J. M. Bryan, *Chem. and Ind.*, 1952, p. 820.
9. Mears, R. B., and Fahrney, H. J., *Trans. Amer. Inst. Chem. Eng.*, 1941, **37**, 911. See also Porter, F. C., and Hadden, S. E., *J. Appl. Chem.* 1953, **3**, 385.
10. D.T.D. 369A.
11. Dummett, G. A., "Materials of Construction", p. 159.
12. Verink, E. D., and Brown, R. H., *Ind. Eng. Chem.*, 1949, **41**, 2095.
13. C.I.O.S. 4/252, 4/253 (H_2O_2 Storage Practice).
14. *Chem. Proc. Eng.*, 1953, **34**, 153.

CHAPTER VIII

COPPER AND COPPER ALLOYS

OF all the metals used for chemical plant, copper has the longest history, and traditional methods still play a great part in its fabrication and use. Small copper parts for stills or reaction vessels are formed by bending or shaping, heated up to soften, and beaten into final form by hand, just as in almost prehistoric days. Coppersmithing is still an honourable and well-defined trade, while the ease and rapidity of hand manipulation will probably ensure its continuance for many years to come. The various brass and bronze alloys derived from copper have almost as long a history, to which the very names—"Admiralty brass", "gunmetal"—testify. As a somewhat unfortunate result, a very large number of copper alloys are available, with properties of no considerable difference as far as corrosion is concerned, while even copper is available in ten or more recognised grades, all containing above 99% of the pure metal.

COPPER

The principal grades of metal specified in this country, with their approximate compositions, are set out in Table VIII–1. The "high-conductivity" grades are produced, as the name implies, for electrical purposes, and are not normally utilised in plant fabrication. The most usual forms met with are the "tough-pitch arsenical" metals (B.S. 1039, 1173), though the "deoxidised" alloys (B.S. 1172, 1174) have been recommended for welded work.

The specific gravity of the soft pure metal is 8·94, and it has an approximate tensile strength of 14 tons/sq. in. The metal work-hardens so rapidly under tests that it is difficult to obtain any exact figure. If a heavily worked hard copper is tested, a proof stress (0·1%) of about 20 tons and an ultimate strength of 25 tons can be obtained. This is at ordinary temperatures, and the metal resoftens at 200°–220° as shown in Fig. VIII–1. As a corollary to this resoftening, the safe load on all forms of copper decreases rapidly as the working temperature is raised. Typical changes are shown in

TABLE VIII-1

Alloy	Alloying Elements (% by weight)	Thermal Conductivity (B.Th.U./sq. ft. hr. ° F. per ft.)	Ultimate Tensile Strength (tons/sq. in.)	
			a.*	h.*
Tough-pitch High-condty. (B.S. 1036)	0·04 oxygen	229	14	20
Tough-pitch (B.S. 1038, 9)	0·10 oxygen	228	14	20
Tough-pitch Arsenical (B.S. 1173)	0·10 oxygen 0·3–0·5 As	102	14	21–23
Deoxidised (B.S. 1172)	0·02–0·08 P	126–175	14	20
Deoxidised Arsenical (B.S. 1174)	0·02–0·08 P 0·3–0·5 As	102	14	21–23
Oxygen-free High-condty.	Traces	229	14	20
Silver-bearing	0·05 Ag 0·04 oxygen	228	14	22
Chromium Copper	0·5 Cr	100	15	29
Tellurium Copper	0·75 Te	208	15	—
Beryllium Copper	About 2% Be with other elements (Co, Ni, Cr)	50	33	75

* a = annealed, h = work-hardened.

Fig. VIII–2, but it is generally recognised that high-conductivity copper should not be put under load at above 150°. Arsenical copper can be used up to 250°, while chromium and silver complexes are reliable to 300°. Copper and all its alloys retain ductility and strength right down to liquid-air temperatures, with a slight increase in Izod values.[1] Unfortunately the most reliable alloys are much less thermally conductive than the pure copper.

The primary impurity found in the metal is oxygen as oxide, left in the process of manufacture. In the process of welding or brazing, these traces of oxide tend to segregate around the copper grains, and give zones of weakness which lead to subsequent cracking. The hydrogen present in flames used for gas welding is absorbed by the molten copper, reacts with the oxide and is liberated as steam as the weld cools. The escaping gas forces the metal grains apart and weld cracking ensues. A neutral-flame technique may check this hydrogen embrittlement, but the oxygen action still continues, and may be enhanced by absorption from the air. Arc welding must therefore be carried out with heavily coated electrodes to give a flux shield, or inert gas screens used. Deoxidised grades of copper, protected from the air in this way during welding, give a much sounder weld than the ordinary metal, and should be specified for all complicated plant handling corrosive liquids. The deoxidation process is not very straightforward, in that hydrogen is absorbed from the reducing furnace atmosphere, and released on cooling, so that the cast metal has a porous structure. However, this porosity disappears on further metal working, and special inert atmospheres can be utilised.

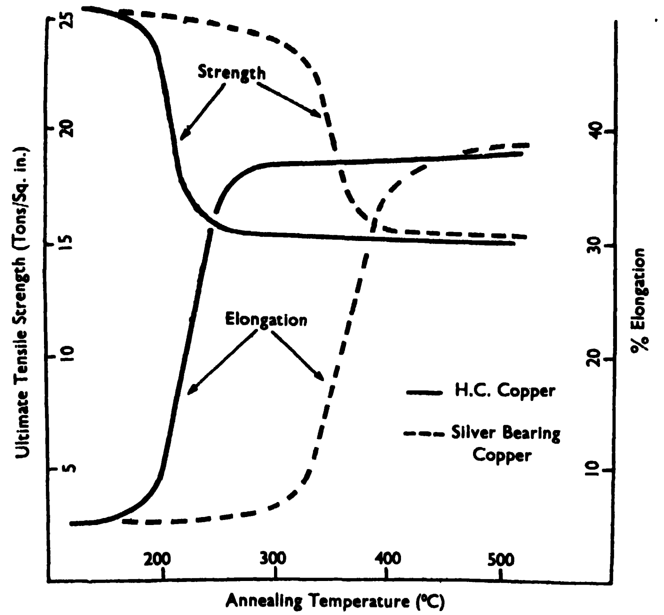


FIG. VIII-1.—EFFECT OF ANNEALING ON STRENGTH AND DUCTILITY.
(After Baker, *Proc. Chem. Eng. Grp.*, 1937, **19**, 41)

The actual deoxidation is generally carried out by adding phosphorus, and as will be seen a residue remains in most of the finished metals. The effect on mechanical properties is slight, but

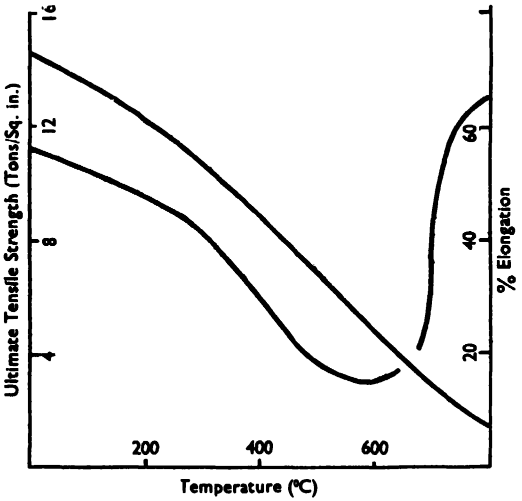


Fig. VIII-2*a*.—Tough Pitch Arsenical Copper Strength and Ductility *v*. Temperature.

(*Courtesy of Copper Development Assn.*)

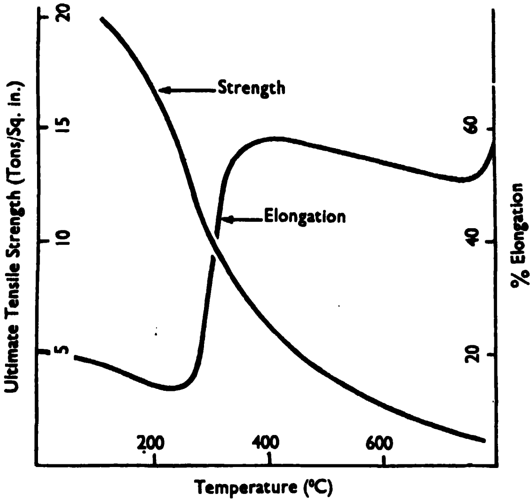


Fig. VIII-2*b*.—Hardened High Conductivity Copper—Tensile Strength and Ductility *v*. Temperature.

(After Baker, *loc. cit.*)

the thermal conductivity drops as the content increases. Arsenic, silver, chromium, and other metals have been deliberately added to increase strength, especially at higher temperatures. Bismuth has not been added, as it is the most undesirable of impurities. A low-melting eutectic with a very high bismuth content is left in any solid alloy as a coating round the higher-melting grains. Sulphur, present in all copper ores, is eliminated completely in manufacture. Calcium is sometimes found in deoxidised high-conductivity alloys, having been used as a deoxidant, but a better method for this is reduction by charcoal in an inert nitrogen atmosphere.

Tellurium copper has been devised for ease in machining without depreciation in electrical properties, and is not of great interest in chemical plant, but the silver alloy is important when tinning, brazing, or soldering are to be carried out. The annealing temperature has been raised by silver addition to 300°–350°, which may be high enough to prevent any local softening during such treatments. In any case the safe load at temperatures above 150° has been greatly increased, as suggested in Fig. VIII–1. Chromium copper is a heat-treatable alloy, which can be quenched from 900°–1000° to give a soft ductile form. The finished shape can then be hardened by heat treatment to a stable metal of high tensile strength. The very strong beryllium copper has sometimes been classified as a bronze, and used for the manufacture of non-sparking tools—the Brinell hardness is in the region of 350.

PLANT FABRICATION

As with aluminium, copper is generally marketed in the form of sheets or tubes,[11] either hard or soft, and in either case easily worked to another form. The Brinell hardness of work-hardened arsenical copper is from 100 to 120, and all ordinary machining processes are possible, though the metal is rather soft. Copper threads should generally be reinforced with solder or brazing, and a riveted joint, though possible, is uncommon. For chemical plant work welded or brazed joints have become almost universal. The former is preferred for severe conditions, but brazing,[2] with a 60/40 copper-zinc alloy, is cheaper and almost as resistant to corrosion. Bronze (copper-tin) and silver (copper-silver) brazing metals have also been used, as more resistant to corrosion than the zinc alloy. They should all retain strength at low temperatures, as distinct from soft solder, but for certainty of working, low-temperature plant should be made with welded joints. Soft solder (lead-tin) is, as always, most unsuitable for any corrosive conditions, but copper is easily soldered and the fabrication of very complicated forms is made relatively easy. Plant for the production of "conductivity" water is made up in heavily tinned copper, and the joints are soft-soldered to prevent the disturbance of the tinned layer.

A very full description of welding methods has been given in a handbook by the Copper Development Association.[3] All methods —gas, metallic, and carbon arc, resistance and inert-gas shield— have been used, but the gas-welding process is almost invariably applied. The drawbacks of oxygen-bearing metal in giving a porous or cracked weld have already been mentioned. If such a metal is to be joined, then it is best to use a carbon-arc process and rely on the carbon monoxide to screen the joint. All the best welding work is carried out with the deoxidised alloys, using some form of gas flame for the purpose.

The welding rod is normally a silver-bearing copper, deoxidised, with some 0·1% of silicon and phosphorus.[4] A flux can be dispensed with but it is perhaps safer to use one, which should be of anhydrous boric acid mixed with sodium phosphate and chloride. The welding flame must be "neutral" and the whole operation should be completed in one pass, even if this entails welding simultaneously from both sides of the sheet (two operators). After welding, the joint should be well hammered to improve the grain structure, even though it is to be annealed later to give ductility. A good weld should have the full strength of the sheet, and an equal corrosion resistance.

Electric-arc welding has not been very successful, due to solution of gases at the high temperature of the arc, and the current required by the high thermal conductivity of copper. Good joints have only been made when the so-called "bronze welding" has been employed. This entails using an alloy with decidedly lower melting-point than the parent parts, but is very useful for many of the lower-melting alloys as well as for copper. Even here the most popular method is by gas, using a slightly oxidising flame, and a 60/40 brass rather than the earlier bronze.[5] As the cast brass has a strength of at least 25 tons/sq. in., the strength of the joint leaves nothing to be desired. A bronze weld builds up considerable thicknesses of metal in a preformed groove, as shown in Fig. VIII–3. Brazing is indistinguishable from this process as a metallurgical operation, but relies on the capillary flow of molten metal into crevices between the two surfaces to be joined, as shown in Fig. VIII–4.

Copper tubing is obtainable in a wide range of sizes, almost always of the jointless solid-drawn type. It is soft enough to make a self-sealing joint, and a number of proprietary unions or pipe junctions are based on this principle (Fig. VIII–5). Connections to gauges and to control mechanisms are nearly always made with copper pipe because of the ease with which the narrower-bore pipes can be bent into shape by hand. High-pressure leads for oxygen, nitrogen, carbon dioxide, and hydrogen are made from thick-walled tube, with joints screwed and soldered, and a good resistance to most natural waters makes the piping very suitable for hydraulic

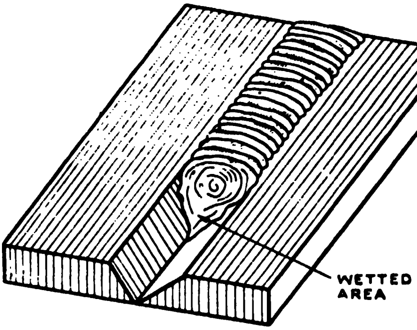

WETTED AREA

FIG. VIII–3.—BRONZE WELDING OF COPPER.
(*Courtesy of Copper Development Association*)

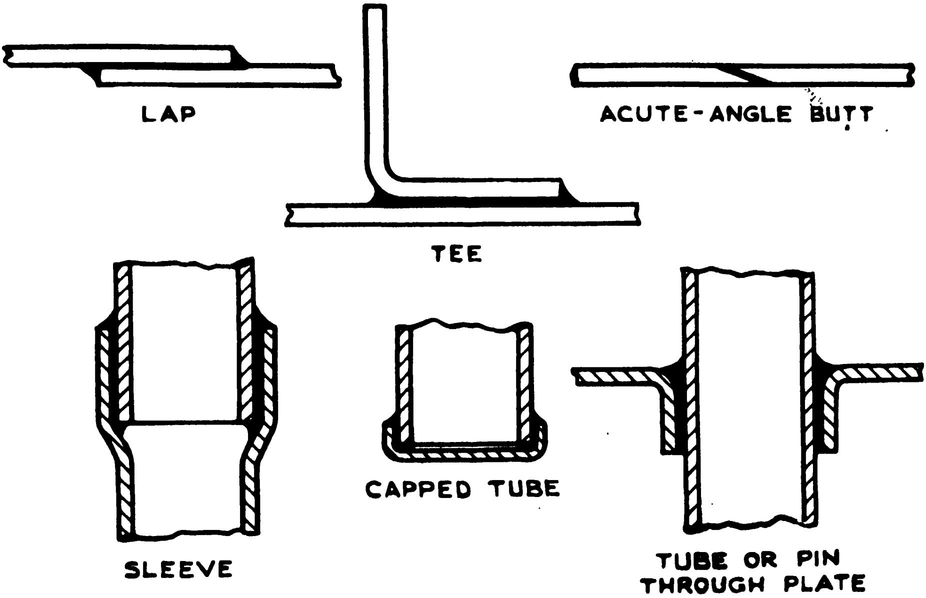

LAP
ACUTE-ANGLE BUTT
TEE
SLEEVE
CAPPED TUBE
TUBE OR PIN THROUGH PLATE

FIG. VIII–4.—EXAMPLES OF COPPER BRAZING.
(*Courtesy of Copper Development Association*)

plant. The last thirty years have seen a gradual displacement of lead by copper in all general plumbing work, although the two can easily be combined by simple "wiped" joints in soft solder. Wall thickness can be calculated from various formulae, but is so important for these widely used conduits that a special boiler insurance formula has been laid down.[6, 11] This gives the limiting pressure P (in lb./sq. in.), in terms of wall thickness (t inches), and internal pipe diameter (d inches), when

$$P = 60(100t - 3)/d$$

Then for a pipe of 2 in. diameter and walls of 0·1 in., $P = 60(100 \times 0{\cdot}1 - 3)/2$, or 210 lb./sq. in. When laying these pipes, some form of relief for water hammer should preferably be provided, and closed lengths should never be left filled with water. Steam-heated plant must be designed to avoid pressures of more than 50 lb./sq. in., even though wall thickness appears quite adequate. Steam-jacketed copper pipes can develop a rounded depression, followed by splitting across the bottom of the bowl so formed, without apparent warning or due cause, if this steam pressure is exceeded. The newer silver-bearing copper can be used for higher pressures.

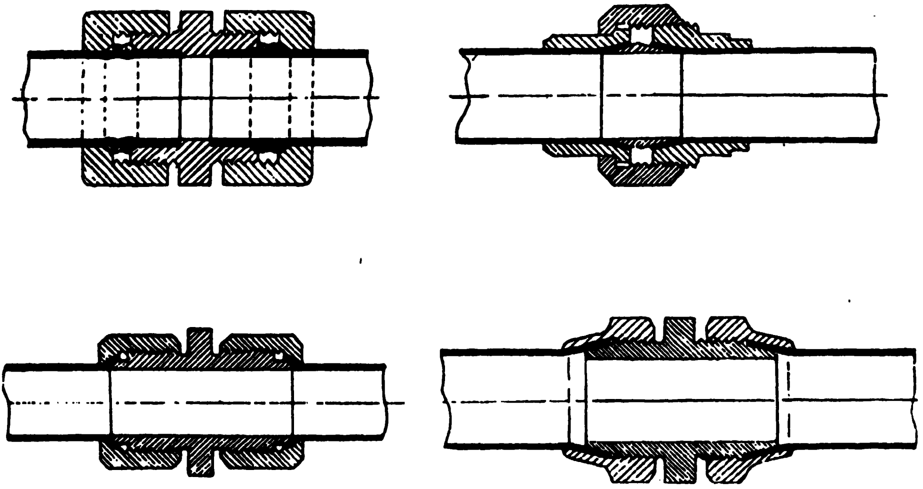


FIG. VIII-5.—SELF-SEALING PIPE JOINTS.
(*Courtesy of Copper Development Association*)

The high thermal conductivity is practically unaffected by temperature changes, and makes toward reducing the size of heat-exchange surfaces. While it is axiomatic that the properties of a metal wall play little part in normal heat-transfer processes, high conductivity is sometimes useful. Consider the design of a kettle for boiling fruit juices, which can be made from copper or stainless steel, each wall being $\frac{1}{8}$ in. thick. Suppose that the heat load is 100,000 B.Th.U. per hour, with a temperature difference of 30° F. The film coefficient for steam might be about 1500 B.Th.U., etc., while the boiling juice will have a value of 1000. Taking the conductivity of copper at 200 and that of stainless steel at 10, the respective wall coefficients become 19,200 and 960 respectively.

$$\text{Then } H \text{ (overall)} - \text{Copper Wall} = \frac{1}{\frac{1}{1500} + \frac{1}{1000} + \frac{1}{19{,}200}}$$

$$= 587 \text{ B.Th.U., etc.}$$

$$H \text{ (overall)} - \text{S.S. Wall} = \frac{1}{\frac{1}{1500} + \frac{1}{1000} + \frac{1}{960}}$$

$$= 370 \text{ B.Th.U., etc.}$$

The surface required will be

$$\text{(Copper) } \frac{100{,}000}{587 \times 30} = 5{\cdot}7 \text{ sq. ft.}$$

$$\text{(Stainless Steel) } \frac{100{,}000}{370 \times 30} = 9{\cdot}0 \text{ sq. ft.}$$

Now stainless steel costs almost twice as much as copper plant of the same size, so the difference in price for the same heat load is very considerable—over three times as much for the steel plant.

This is, of course, an extreme example, but does illustrate the saving that may be made when the very high conductivity is fully utilised. There is also the advantage that a copper wall is almost even in temperature throughout; there are no "hot spots" and the outer surface of a directly heated vessel never rises much above the inner and cooler sections. Coal-fired copper boilers are still used for brewing, perhaps by tradition, but working brewers claim that the metal gives an even and vigorous boil. The extensive use of copper in locomotive fire-boxes illustrates how completely the metal is held to boiling water temperature, even at very high heat-transfer rates.

COST OF COPPER PLANT

As with stainless steel, the bulk of the cost is in the metal. With world prices largely determined by United States policy and internal British prices fixed by Government control,* it is clearly impossible to give any firm figure for any long period. The present world price on a free market is 30 pence per pound, but the British internal price is slightly less at 28·5 pence (September 1952). Copper tubes and sheets will usually cost 4*d.*–5*d.* more than the block metal, and with fabrication costs varying from 8 to 24 pence per pound, it may be expected that the finished plant will be priced at 3*s.* 6*d.* to 5*s.* per pound (£420 to £600 per ton).

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* Now a free market—Sept. 1953.

RESISTANCE TO CORROSION

The fundamental mechanism whereby the metal resists attack would appear to be a high overvoltage of hydrogen discharge, which makes simple hydrogen liberating reaction almost impossible. When oxygen or oxidising agents are present, the cathodic points are depolarised, and corrosion proceeds much more rapidly, at a rate determined by the solubility of copper compounds in the corroding solution. Thus, in neutral conditions, cuprous hydroxide or related compounds will be precipitated around the anodic areas, and confer a very considerable degree of protection. The wide use of copper roofing, which can give service for hundreds of years even in heavily polluted atmospheres, is a proof of this inhibition. The green colour or "patina" of copper roofing is due to a mixture of basic sulphates and carbonates, with some chloride in seaboard deposits. Provided that this deposit is undisturbed, attack on the underlying metal becomes very slow. The author has examined a church roof which was in such excellent condition after seventy years' exposure to London atmospheres that no apparent change in thickness had taken place from the original sheet. At the same time, a rainwater spout impinging at one point on the same copper sheet had cut it completely through in a much shorter time. Attack in this case was due to the dissolution or erosion of the anode product combined with easy discharge of hydrogen. When a soluble anodic compound can be formed, there is always a danger of rapid attack on the metal, and copper, unfortunately, tends to form a number of complex ions such as the cuprammonium compounds.

As would be expected from these circumstances, the effect of aeration on all corrosion rates is very marked. Thus a 25% solution of sulphuric acid in air-free conditions only attacks the metal at a rate below 35 mdd, but if air is bubbled through, the corrosion rate goes up at once to 850 mdd. Somewhat similar results are given by phosphoric and hydrochloric acids, and this behaviour makes the resistance of all plant somewhat uncertain. A unit in continuous operation, from which air is excluded, can operate successfully for years, while a batch plant, with intermittent shut-down and aeration, may be put out of action in a few months.

Copper is markedly cathodic to iron, aluminium, zinc, and many alloys. As a result, combination with these metals may lead to rapid selective attack, checked in part by hydrogen overvoltage. Copper sheathing fastened with nails is unusual in chemical plant, but if used, the attack on iron nails destroys them in a few months, even if exposed to nothing worse than wind and weather. Copper and aluminium should never be in metallic contact in any piece of plant, and the same limitation applies to the various copper alloys. At the same time, copper tubes are often expanded into steel tube-plates for evaporator construction, and do not appear to set up the corrosion cells which are theoretically possible. A typical evaporator known to the author has been retubed three times in twenty years, but the original tube-plates are still in excellent order. They are probably protected by a thick and stable oxide layer, while there is not sufficient air present in the steam for a rapid depolarisation of the copper.

Resistance to Acids

Sulphuric acid, in the cold and unaerated, has little action, but as soon as the temperature exceeds about 50° the acid itself can act to depolarise the cathodic areas. Then, as copper sulphate is very soluble, there is nothing to check reaction, which can become violent. If the acid contains traces of oxidising salts, corrosion can be very marked even in the cold. A running water with 0·1% H_2SO_4 + 0·006% of ferric sulphate will attack copper fittings at rates up to 200 mdd. Copper racks have been used for iron castings in an acid pickling bath, but here in addition to strongly reducing conditions the iron was conferring cathodic protection. Monel metal would have been vastly better for such work. Generally, then, copper should not be used in the presence of sulphuric acid solutions.

Nitric acid in any concentration attacks copper at once, as does nitrous acid or nitric oxides. The metal cannot be used for handling free acid and all nitrates should be avoided.

Hydrochloric acid solutions are too corrosive for normal use, with rates of attack reaching 200 mdd even when the HCl concentration does not exceed 1%. The action is not violent, however, unless hot concentrated acid is concerned or an oxidising agent is present. Feebly acid solutions containing chlorides have little action unless aerated, as shown by the general use of copper in glycerine-salt lye evaporators. Chlorine or the oxyacids of chlorine will of course function as oxidising agents and cannot be tolerated in solution. Dry chlorine is stable enough, and liquid chlorine at low temperatures is safely handled in copper piping. Hydrofluoric acid is not so active as HCl, and the metal has been recommended as a possible alternative to Monel for all strengths of this acid.[7]

Neutral or slightly acid salt solutions with no oxidising properties can generally be handled. Even ammonium salts, which might be made an exception, are sometimes evaporated and crystallised in copper plant, though the practice is somewhat dangerous. Copper salts themselves, including the nitrate, are safely made in the metal, as the tendency to "plate out" and form local cathodes is thereby removed. Sulphites and sulphurous acid are a little unstable, but copper has been recommended for sulphite pulp in paper manufacture.[8]

Basic Solutions

The resistance of copper to all alkalies, with the exception of ammonia, is very good. Ammonia in any concentration will attack the metal at once, and forms with nitric acid the pair of substances that should never be brought into contact with copper plant. The reaction is through the formation of a cuprammonium complex, and can be simulated by substituted ammonium compounds. Alkaline cyanides will also dissolve the metal as a complex ion. On the other hand, caustic soda, in concentrations up to about 50%, can be filtered boiling through a copper gauze without any sign of attack. Rates of corrosion by ammonium salts are reduced in the presence of sulphides, curiously enough.[13]

Organic Acids

Copper was the first material available for boiling acetic acid solutions, and soon established a wide reputation in the handling of almost all other solutions of the same type, especially where a trace of colour was not an objection. Rates of attack rarely exceed 100 mdd, even when the solutions are boiling, unless some oxidation can occur. It is fairly safe to use copper for any form of oxygen-substituted organic compound, even when the halogens are also present. Unfortunately many develop a deep green colour, even when the rate of attack on the metal is negligible. This has led to the gradual replacement of copper by the slightly less stable but non-staining aluminium. Copper does not show the "anhydrous" attack characteristic of the other metal, but high-boiling acids really require a molybdenum-bearing stainless steel.

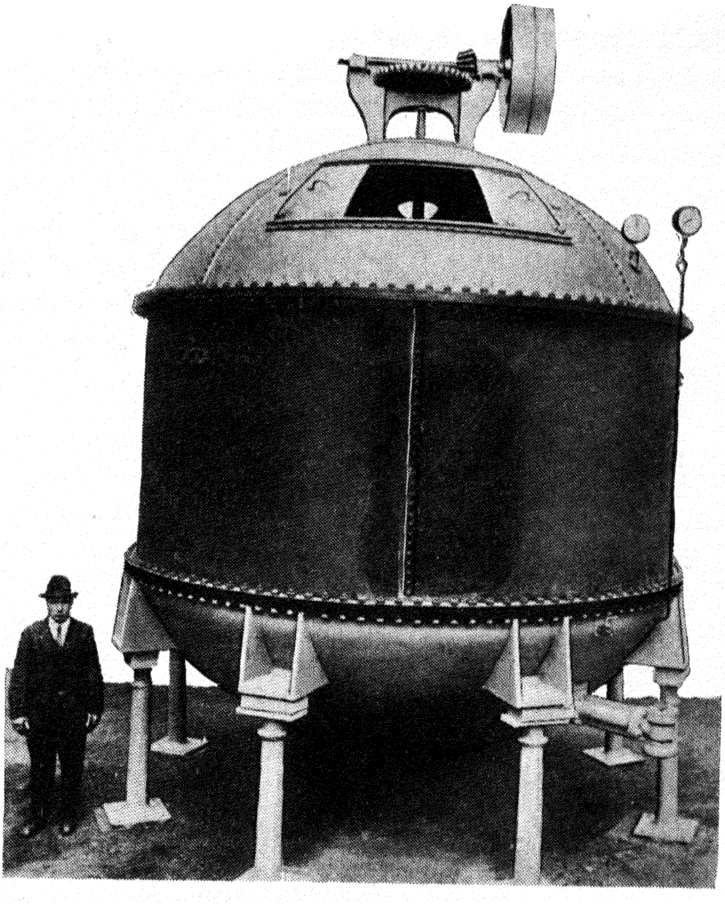

FIG. VIII-6.—LARGE COPPER BREWING VESSEL.
(*Courtesy of Blairs, Ltd.*)

Copper has been widely used for all food products, and the relative toxicity of this and other metals has frequently been a matter of dispute. Brewing and spirit distillation has long been a field in which copper is very widely used, and the tradition is so strong that it will be difficult to introduce any alternative material. It cannot be said that the metal is inert to micro-organisms, as the use of copper sheathing for ships is based upon the poisoning of all marine life, but brewing vessels such as that shown in Fig. VIII-6 are generally used in fermentation processes. It is easy to maintain the plant in a sterile condition, owing perhaps to this very toxicity, and the traces of copper dissolved in the process may definitely contribute to other reactions.

Tinned copper is dealt with under the sections dealing with tin, but is a valuable supplement to the base metal for handling all types of foodstuff. Copper-clad aluminium, made by normal hot-rolling, has been used in electrical work, but the alarming possibilities of electrolytic coupling should keep the combination out of chemical plant construction.

COPPER ALLOYS

These are the alloys containing more than 50% of copper, introduced in large numbers over very many years to overcome the softness, low tensile strength, and high casting temperature of the pure or nearly pure metal. Space does not permit of the mention of more than a few of the characteristic members of each class.

Brass

Four typical copper-zinc alloys are specified in Table VIII–2. As will be seen, the high thermal conductivity of copper has disappeared but the metal is appreciably stronger, even in a soft form, and hardens rapidly to a 0·1% proof stress of almost 30 tons/sq. in. The strength and ductility are well maintained over a range from 300° to −180° C., and brass castings are easy to make, with no gassing troubles. The metal is easy to machine, and with a Brinell hardness range from 55 to 200 is quite hard enough for all forms of screw-cutting and similar operations.

TABLE VIII–2

Name and B.S. Number	Composition (%)	0·1% Proof Stress (tons/sq. in.)	Conductivity (B.Th.U./sq. ft., etc.)
Cartridge Brass (267, 378)	70 Cu, 30 Zn.	(a) 5 (h) 28	57
Admiralty Brass (378)	70 Cu, 29 Zn, 1 Sn	(a) 5	
Naval Brass (1541, 409)	62 Cu, 37 Zn, 1 Sn	(a) 8	43
Muntz Metal (1541, 264)	60 Cu, 40 Zn	(a) 8	52

These alloys are not so corrosion-resistant as copper, despite the fact that they exist as a single solid phase (with the possible exception of Mentz metal). They are particularly subject to a preferential attack on the zinc component (dezincification), which is dissolved out to leave a porous mass of copper, with no appreciable strength or even watertightness. No more corrosive agent than ordinary soft water containing dissolved air and carbon dioxide is required, though sea water is much more destructive. Any irregularity in the surface is prone to form a nucleus for localised attack, and the points at which the brass pipes are screwed into fittings or expanded into tube-plates are particularly subject to reaction. At these points also there is often a local turbulence sufficient to give erosion of protecting films and other forms of local attack.

Failures due to dezincification or to corrosion-erosion have been particularly marked in the condensers fitted to marine engines, and according to Mr. Winston Churchill caused more damage to the British Grand Fleet in the 1914–18 war than all enemy action. In the years following much experimental work showed that traces (up to 0·1%) of arsenic checked zinc removal almost entirely, while the incorporation of 2% aluminium gave a brass much more resistant to erosion. As a result condenser tube trouble was almost entirely absent during the 1939–45 period of hostilities.[9] For very long wear, however, the more costly cupronickel tubes (below) are being introduced.

Brass behaves generally as copper in chemical plant, with somewhat greater rates of attack. It has no marked polarity relative to the latter and is freely used for valve metals, or for the cast sections in a copper plant, to which it can be joined by brazing. Although the relatively soft seat makes it easy for water valves to be made entirely in brass, it is not so suitable for hot liquids or vapours. Wet steam will cut a groove across a brass valve seat in a matter of hours, and bronze or copper-nickel alloys should always be used for such work. Brass tubes are particularly subject to corrosion cracking, and a special test with mercurous nitrate has been recommended.[12]

The cost of brass in its various forms is about the same as copper, though tin-bearing alloys will reflect the present high price of this metal (about £950 per ton).

Bronze

This was the name given originally to copper-tin alloys containing up to 10% of the latter. Small amounts of phosphorus are sometimes added to deoxidise the metal, and in residual amounts to harden the finished alloy; mixtures treated in this way are known as phosphor-bronzes, even though the amount of phosphorus left is too small for notice. Zinc is an alternative to phosphorus, and gives the gunmetal range of alloys. Table VIII–3 sets out the principal characteristics of this group.

TABLE VIII–3

Name and Specification	Composition (%)	0·1% Proof Stress (tons/sq. in.)	Conductivity (B.Th.U./sq. ft., etc.)
Low-Tin Bronze (B.S. 407/1)	96 Cu, 3·5 Sn, 0·1 P	7 (a)	58
Tin Bronze (B.S. 407/2)	94·5 Cu, 5·25 Sn, 0·1 P	8 (a)	43
Phosphor-Bronze Casting (B.S. 1400)	90 Cu, 10 Sn	8 (a)	29
Gunmetal (Leaded) (B.S. 1400)	85 Cu, 5 Sn, 5 Zn, 5 Pb	6 (a)	42

The proof stress given above is for the annealed metals, which on cold-working develop a very high strength (up to 60 tons/sq. in.) and hardness. They are particularly suitable for wire drawing or for valve construction, being generally harder than the brasses and not subject to differential corrosion. Lead-bearing alloys are said to corrode rather more rapidly than those containing only tin and copper, but apart from this all bronze alloys can be used with confidence wherever copper has resisted corrosion. The same agents (HNO_3, NH_3, etc.) which give rapid attack on copper will also attack bronze, but the corrosion may not be so severe. Dilute sulphurous acid, in particular, is almost completely inert, and bronze is a useful supplement to lead or stainless steel.

The cost of all tin alloys will largely be determined by the price of tin, which has varied to an extraordinary degree over the last ten years. From 1950 onwards the price has seldom been much below £1000 per ton. A basic price for phosphor-bronze would thus be about 40 pence per pound, while prefabrication charges will be about the same as for copper.

Aluminium and Silicon Alloys

These are commonly known as aluminium or silicon bronzes, though no tin is present. Of relatively recent development, they show considerable advantage for chemical plant work, especially at elevated temperatures. Details are set out in Table VIII–4 below.

TABLE VIII–4

Name	Composition (%)	0·1% Proof Stress (tons/sq. in.)	Conductivity (B.Th.U./sq. ft., etc.)
Aluminium Bronze	93 Cu, 7 Al	8 (a)	44
Aluminium-Bronze Casting (B.S. 1410)	86 Cu, 10 Al, 2 Fe, 1 Ni, 1 Mn	11 (a)	30
Silicon Bronze	96 Cu, 3 Si, 1 Mn	6 (a)	20
Silicon-Bronze Casting	90+ Cu, 4 Si, with Fe, Zn, Mn	—	—

The aluminium-bearing alloys retain their strength remarkably well at temperatures up to 400°, while the silicon bronzes actually improve in both strength and ductility as the temperature rises from 20° to 200°.[10] All work-harden rapidly to strengths of the order of 40–50 tons/sq. in., combining this with easy welding and good machining qualities. Full strength and ductility are maintained at low temperatures also, at any rate for the aluminium alloys.

In corrosion resistance they appear to behave at least as well as the true bronzes. A silicon bronze will resist all strengths of sulphuric acid in the cold, and up to 70% when boiling, though it has been claimed that high-pressure steam is able to attack at grain boundaries. The aluminium bronzes are widely used in paper-making for resisting all the solutions encountered, and are fabricated into autoclaves for fatty acids. It is possible to use these instead of the more expensive cupronickel alloys for many purposes.

Cupronickel Alloys

The range of copper alloys which contain from 5% to 30% of nickel are perhaps the best of all for strength and resistance to corrosion. They represent a halfway stage between copper and Monel metal, with the relative cheapness of the former and the corrosion resistance of the latter. A number of different mixtures have been tried, of which Table VIII–5 makes an arbitrary selection of three. The 70/30 mixture, combined with 1% Fe, 1% Mn, is the Admiralty cupronickel mixture, and has been widely adopted for all condenser practice where long periods of trouble-free service are essential.

TABLE VIII-5

Composition (%)	Proof Stress (tons/sq. in.)	Thermal Conductivity (B.Th.U./sq. ft., etc.)
90 Cu, 10 Ni, +1 Fe	7·5 (a)	26
80 Cu, 20 Ni	7·0 (a)	21
70 Cu, 30 Ni	10·0 (a)	17

Corrosion resistance is higher than with the bronzes, but the high copper content means that there will be obvious weakness in oxidising conditions. The action of cold unaerated sulphuric acid is negligible at all strengths, but cold aerated acid, even at 5% H_2SO_4 will corrode at rates up to 600 mdd. Hydrochloric acid behaves in the same way, with slightly higher attack by the cold acid, but hydrofluoric acid is inert. Organic acids, in non-aerated solutions, can all be handled except at the highest boiling temperatures, and there is some resistance to free ammonia. Cyanides and perhaps sulphides are still too active to be handled in these cupronickels, while the salts of heavy metals such as silver and mercury plate out and set up local corrosion cells.

Atmospheric attack is negligible up to about 400°, and the metal will resist high-pressure steam much better than the bronze range. Dry halogens, with the possible exception of iodine, do not attack, but when moist, corrosion rates become uneconomic. Cupronickel has been suggested for handling hypochlorite bleach liquors, but better materials, such as rubber in its various forms, are available.

The cost of cupronickel must reflect the higher price of the second ingredient (£450 per ton in 1952). There is little demand for sheet, and the solid-drawn tubes sell at about 3*s*. per pound.

REFERENCES

1. Colbeck, E. W., *Trans. Inst. Chem. Eng.*, 1949, **27**, 55.
2. B.S. 1723; 206.
3. Copper Development Assn. Publication 47, "The Welding of Copper, etc.".
4. B.S. 1077.
5. B.S. 1724.
6. See, e.g., Baker, S., *Proc. Chem. Eng. Grp.*, 1937, **19**, 41.
7. Imperial Smelting Corpn. Handbook, "Acid Handling", 1950.
8. Copper Development Assn. Publication No. 23, "Copper in Chemical Plant".
9. Evans, U. R., *Chem. and Ind.*, 1951, p. 706.
10. Boodson, I., and Davis, E., "Materials of Construction", p. 173.
11. B.S. 378 (1953).
12. B.S. 885 (1953).
13. U.S.P. 2,522, 430.

CHAPTER IX

NICKEL AND NICKEL ALLOYS

NICKEL

The first point to be made is that the ingot metal costs 3*s.* 9*d.* per pound and a rolled sheet 4*s.* Prices are rising slowly and steadily, and supplies are short all over the world. This may be a temporary state of affairs, but it has persisted for the last twelve years and seems likely to continue for a considerable time. Assuming that units will never be very large, the fabrication costs will add from 1*s.* to 3*s.*, making a total cost for the nickel plant of 5*s.* to 7*s.* per pound. Such charges, coupled with the fact that nickel is not particularly resistant to acids, would almost rule out use were it not for the fact that nickel-clad sheet is fairly easy to produce. The composite sheet is produced by the normal method of hot-rolling, producing a pair of metals which, though firmly cemented together, are quite distinct, as shown in Fig. IX–1, the nickel retaining all its characteristic properties. The two metals, moreover, are very similar in mechanical properties, and the total sheet thickness is available for stress resistance. Reasonably wide use of nickel has been made possible by the use of this composite material.

Nickel, as accepted for commercial purposes, normally contains less than 0·5% of metallic impurity, with a carbon content that varies from 0·02% to 0·10%. This has the same effect as with iron, hardness of the annealed metal increasing with content, but the change is not so marked. The essential mechanical properties of a typical sample are set out in Table IX–1.

TABLE IX–1. PROPERTIES OF COMMERCIAL NICKEL

Specific Gravity	8·9	Ultimate Tensile Strength, hardened	60 tons/sq. in.
Melting-point	1435°–1455° C.	Izod Impact Test (ft.lb.)	70–85
Brinell Hardness	75–150	Thermal Conductivity (B.Th.U./sq. ft., etc.)	100° C. 35 490° C. 31
Proof Stress (0·1%) annealed	8 tons/sq. in.		

All normal grades work-harden rapidly, as suggested by the figures above, and the ductility persists over a wide range of temperatures, up and down. A grade for casting can contain up to 3% of alloying elements, mainly silicon, while a manganese-bearing metal is sometimes recommended for higher resistance to sulphur. All these can easily be machined with the same tools and equipment as for mild steel. Strips, rods, tubes and sheets are available, within limits, and the special sections required for any chemical plant can be built up by homogeneous welding. Joints may be made by any form of soldering, brazing, gas or electric-arc welding, and, of course, by screwing, threading, and tapping. A gas weld gives a better structure than arc welding, as can be seen in Fig. IX–2. If the clad sheet is used, then a double weld is necessary, and this will, of course, increase the cost of plant. It may be possible to put a "loose"

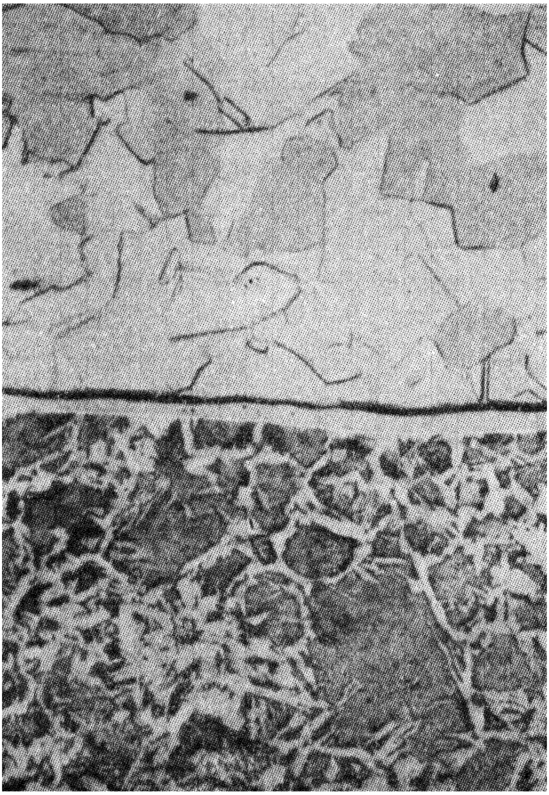

FIG. IX–1.—PHOTO-MICROGRAPH OF NICKEL-CLAD STEEL.
(*Courtesy of Henry Wiggin & Co., Ltd.*)

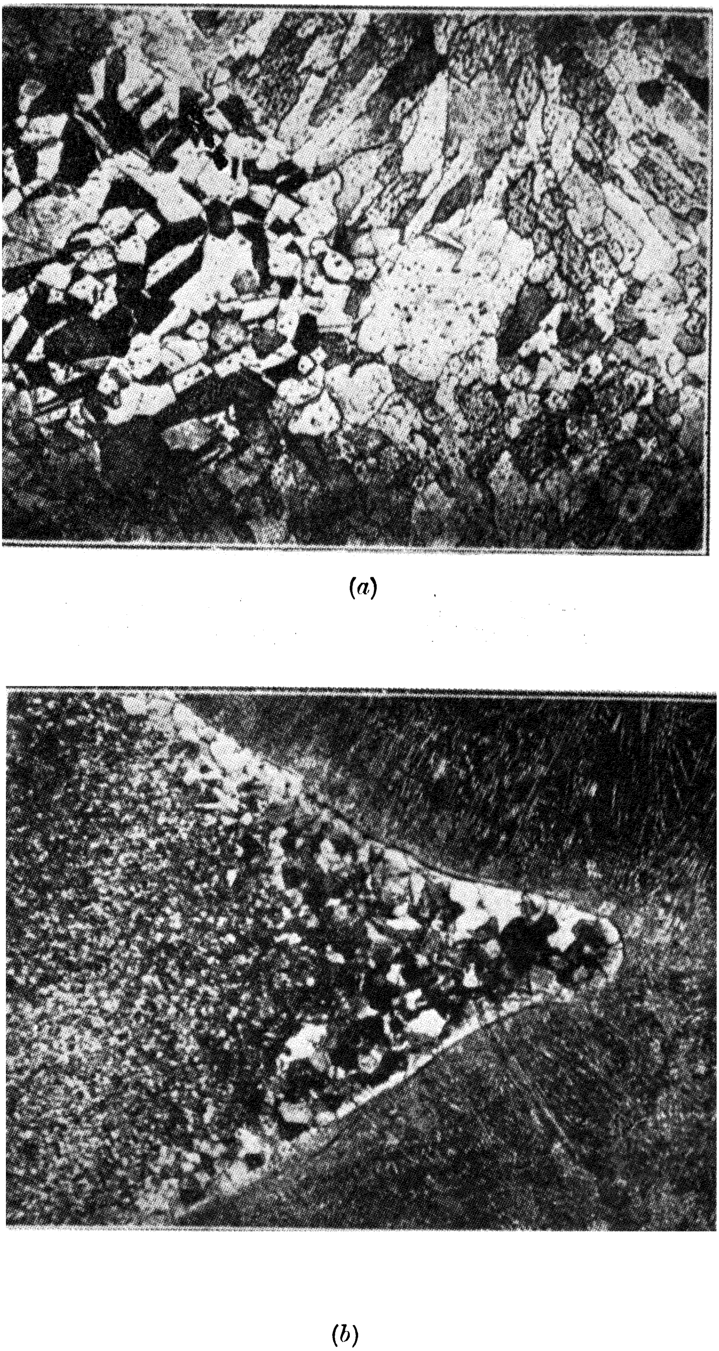

FIG. IX-2.—MICRO-PHOTOGRAPHS OF NICKEL WELDS (× 25).

(a) Oxy-acetylene Weld.
(b) Metallic Arc Weld

(*Courtesy of Marshall, W. K., Trans. Inst. Chem. Eng.*, 1944) lining of nickel into a steel tank by welding strips at the edges, or by "plug welding" with holes drilled in the nickel sheet. There seems to be no difficulty in welding nickel direct to steel in such cases.[1]

Corrosion Resistance

The mechanism of corrosion appears to follow closely on that of copper, with difficulties of hydrogen discharge controlling. The metal has a higher solution potential than copper, while the overvoltage for hydrogen discharge is a little lower. As a result, it can be expected that acids capable of forming soluble salts will corrode, while the effect of alkalies is dependent on the formation of more or less stable oxide films. This is in fact found to be the case, with a very firm and resistant skin forming in the presence of caustic alkalies. Except for one or two particular cases, nickel shows no improvement over copper and copper alloys for handling acids.

Attack by all concentrations of caustic soda, at any temperature to boiling-point, is small, and nickel is better than any other metal with the exception of silver. Almost anhydrous alkali can be produced in nickel evaporators such as that shown in Fig. IX–3 with a metal content of less than 2 parts in 10 million. Tubes, tube-plates, and ebullition chambers can all be made in nickel, the mechanical properties of which are admirably suited to such construction. Hard-drawn tubes are expanded into relatively thin tube-plates, and the shells built up from ¼-in. sheet by arc or gas welding.[2] A pure caustic soda has no action, but attack may be set up in the presence of chlorates or sulphides.[12] As a sharp distinction from copper, ammonia, in solution or as hot gas, has no action, and nickel is often used for the ammonia side of heat interchangers on nitric acid plants. There is some slight attack on the metal by a hot aerated ammonia solution, but there is no reason to use nickel where mild steel is adequate.

The only advantage of nickel over copper in handling acids is the relative lack of colour of the corrosion products and the non-staining characteristics of the metal. As a result nickel is often used in the preparation of slightly acid foodstuffs, where both metals are almost inert unless aerated, and copper may give "off-colour" products. Traces of nickel are definitely non-toxic, and milk, which must be without suspicion in this respect, is normally handled in nickel or Inconel (below). Moulds and bacterial growths are not affected and sea water can cause corrosion by pitting the areas below unpoisoned barnacles—as with stainless steel. Hydrogen peroxide is reasonably stable, and the peroxide bleaching tanks of the textile industry have been made in nickel-clad steel. This may not be wise in view of the fact that oxidising conditions promote corrosion.

Most strong acid solutions will attack nickel at a greater rate than for copper or Monel metal, and in these circumstances it is seldom used. Perhaps for hydrochloric acid and organic chlorides nickel is to be preferred, either because of discoloration effects (aniline hydrochloride, carbon tetrachloride) or because of specially low corrosion rates (phosphorus oxychloride and tricresyl phosphate). Delicately tinted polymers containing phenols are often made entirely in nickel plant, while the many solutions of the artificial silk industry may need a metal free from either copper or iron but harder than aluminium. Apart from this colouring effect, it is doubtful if nickel will ever replace the cheaper alloys.

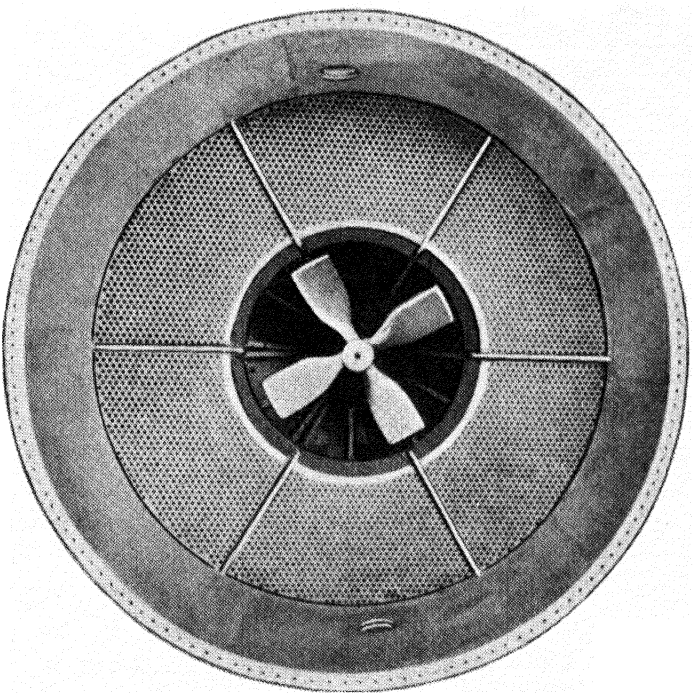

FIG. IX-3.—SECTION OF 24 FT. DIAM. NICKEL EVAPORATOR.

(Courtesy of Manistee Iron Works and Bureau of Information on Nickel)

MONEL METAL*

This is the most important nickel alloy used in the chemical industry, and in fact is the most important in nearly every field. Prepared direct from many natural ores, it contains the two metals (nickel and copper) in approximately the right proportions of 2 to 1, and the final mix is adjusted to the standard proportions given below in Table IX–3.

TABLE IX–3. COMPOSITION AND PROPERTIES OF MONEL METAL

Composition (% by weight)	Nickel 68–70 Copper 28–29 Manganese 1·0–2·5 Carbon 0·05–0·1	Iron 0·2–2·0 Magnesium 0·1 Sulphur 0·005–0·008
Ultimate Tensile Strength (tons/sq. in.)	Room Temp., 37 200° C., 33 400° C., 32	500° C., 28 600° C., 20 700° C., 14
Thermal Conductivity (B.Th.U./sq. ft., etc.)	94° C., 15 288° C., 15·7 439° C., 18·8	
Hardness	Brinell No. 120–250	
Izod Impact Value	65 (Hard)	115 (annealed)

As will be seen, this is a mechanically reliable metal with a very wide range of working temperatures; not only is the strength retained up to over 600°, but the Izod impact value is practically unchanged right down to —180°.[3, 4] The annealed metal is as hard as ordinary steel, and can be work-hardened to a very good wearing surface. This allows wire-drawing to almost any degree of fineness, and the wires so obtained can be woven into metallic cloths of high strength and chemical resistance. Machining follows ordinary techniques, but the machined surface is harder than mild steel and requires first-class tool steels for successful manipulation. When much machining is required the carbon content should be kept below 0·1%, and in any case the lower carbon content is preferable for chemical work. It is not possible to heat-treat the metal for hardening, only cold-working giving the harder forms. The annealing range is from 630° to 820°, and the lower limit might be considered as the maximum working temperature for Monel plant.

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* "Monel" is a registered trade mark.

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In order to confer heat-treating qualities on the alloy, some 3% of aluminium is introduced, giving the so-called "K" Monel. The metal is softened by quenching from about 900°, worked to shape at a Brinell hardness of about 160, and then heat-tempered at 580° to give a final hardness of 300–340. As hardness is accompanied by a tensile strength of over 70 tons/sq. in. at ordinary temperatures, only dropping to 36 at 650° and 14·5 at 800°, the alloy has great mechanical possibilities.[5] It is without magnetic properties at any temperature. In order to make a good casting metal it is usual to add 4% of silicon, forming the "H" and "S" Monels, and neither this silicon nor the aluminium of "K" seems to have any notable effect on corrosion resistance.[14] At the same time, they provide a group of metals of slightly different composition, which can "run" easily on each other and are particularly suitable for the individual parts of pumps or valves.

The alloys are slightly cheaper than would be expected from their nickel content, sheets and tubes costing about 3*s.* 3*d.* per pound at the present time (September 1952). As they are not very easy to build into plant, a construction charge of 1*s.* 6*d.* to 2*s.* 6*d.* will bring the total cost to just under that of nickel. Monel clad steel is available.[15]

Monel can be welded to give a joint of strength equal to the original sheet. As with all copper alloys, the weld should be kept from exposure to oxygen, and it is probable that a gas weld will be preferable to an arc weld, though both are possible.[5]

Corrosion Resistance

This is better than for either of the principal constituents. Nickel is higher in the electrochemical series than copper, and may be more effectively protected by oxide films, while copper is primarily screened by hydrogen overvoltage. Monel appears to profit from both effects, in that it is not so much attacked by acids as nickel, while the complex ions which lead to copper corrosion are no longer formed. On the other hand some local attack at welds due to the presence of two metals has been noted.[16]

As a result, all dilute mineral acids—even nitric—have no appreciable action when cold and below 1% in strength. Oxidising conditions do increase corrosion, and the handling of HNO_3 is not really desirable, becoming quite impossible when concentrations of above 5% are reached. On the other hand, 5–10% hydrochloric acid, even if hot, can be in contact with Monel for long periods without serious damage. This is particularly important in the design of hooks and racks for acid pickling plant, where the metal is partly protected by steel or cast-iron surfaces being "pickled". The action of dilute sulphuric acid is still less, as can be seen from Fig. IX–4. The photograph shows a pickling "skip" which has been in continuous service for seven years raising iron castings in and out of 10% H_2SO_4 at 80° C. Monel can in fact be used for all strengths of sulphuric acid up to 50%, at temperatures in the region of 100°, as shown in Fig. IX–5, provided air is substantially absent. Traces of arsenic in the acid act as a useful inhibitor, 0·2% by weight reducing attack in the range 50–70% H_2SO_4 by 90% or more.[6] The rapid increase in corrosion as the acid strength goes beyond 60% can thus be "postponed", and a strength reached at which cast iron can take over, so giving an entire range of lead-free material for handling

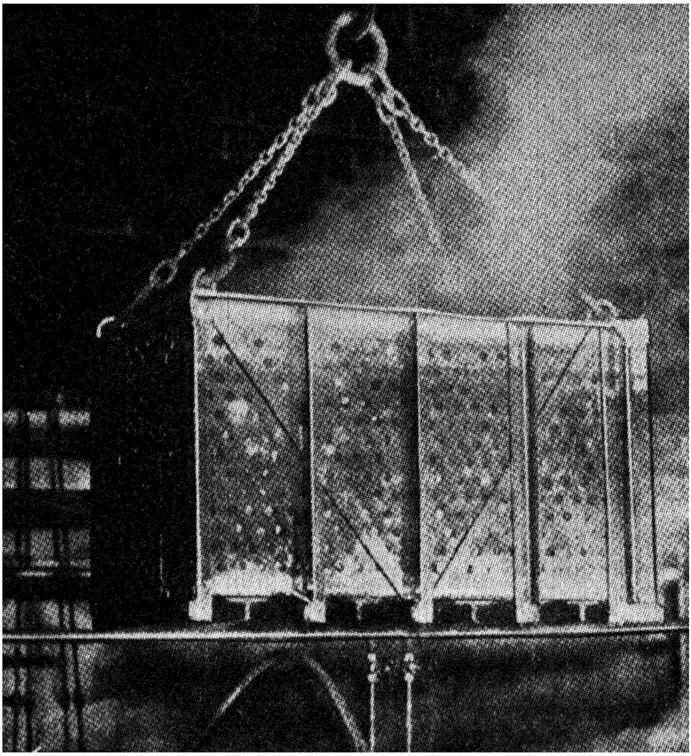

FIG. IX–4.—MONEL METAL PICKLING BASKET (AFTER 10 YEARS' SERVICE).
(Courtesy of English Steel Corpn. and Henry Wiggin & Co., Ltd.)

sulphuric acid. Table IX–4 shows how Monel compares with other acid-resistant materials in resistance to boiling sulphuric acid.[7]

TABLE IX–4

CORROSION OF METALS BY BOILING SULPHURIC ACID SOLUTIONS *
(inches per year)

Metal	Acid Strength (% by weight H_2SO_4)					
	5	10	19	50	75	96
Monel . . .	0·0034	0·0024	0·0075	0·065	2·3	3·3
Nickel . . .	0·034	0·12	0·11	3·4	0·9	2·3
Inconel . .	0·24	0·39	0·64	7·8	4·8	0·86
Chemical Lead .	0·016	0·015	0·042	1·2	(specimens destroyed)	—
Antimony Lead .	0·016	0·019	0·046	0·023	0·57	—
Tellurium Lead .	0·025	0·021	0·035	0·023	0·092	36·3
Ni-resist . .	0·51	1·31	2·1	2·5	2·4	3·1

* "Monel *v.* Sulphuric Acid."

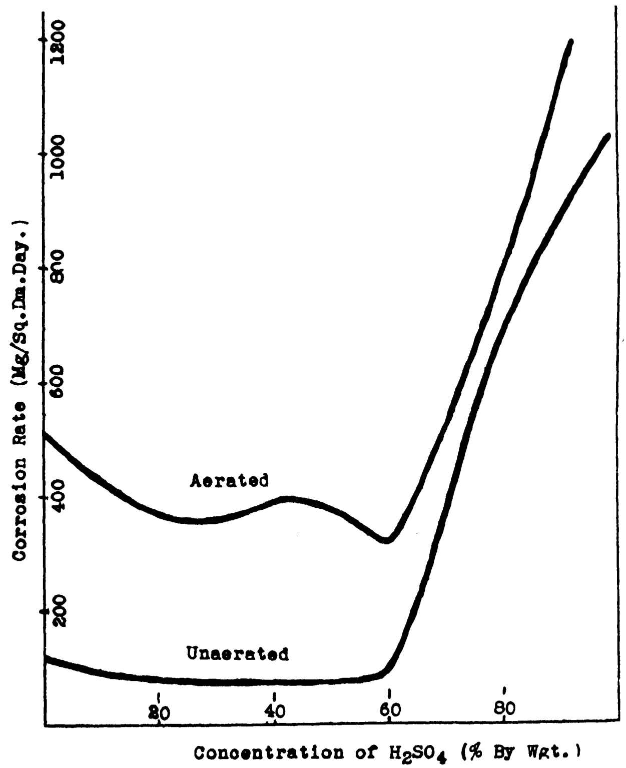

FIG. IX–5.—CORROSION OF MONEL METAL BY HOT SULPHURIC ACID (95° C. VELOCITY 16·5 FT./MIN.).

(Courtesy of Henry Wiggin & Co., Ltd.)

Inertness to phosphoric acid is quite satisfactory, with rates of corrosion below 50 mdd unless the acid is aerated. Unfortunately a crude phosphoric acid will often contain ferric or other oxidising salts, and these will promote attack just as with copper or nickel. This oxidising salt effect is one of the shortcomings of Monel as compared to Inconel or one of the stainless steels. An iron-free aluminium sulphate solution attacks at rates below 10 mdd, even at boiling-point, but the traces of iron present in a crude salt made from bauxite raise this figure to nearly 100. Curiously enough, Monel has been recommended for the manufacture of sodium bichromate. Resistance to dry chlorine, bromine and fluorine, or to their halides, is good, and the metal has been used widely for valves and pipe lines. Complex halides, such as thionyl chloride, are generally inert.

The resistance of Monel to all forms of alkali is very good, being only second to nickel or silver. Ammonia in solution has no visible effect, and only when exposed to the hot dry gas does the alloy reveal any weakness. Caustic alkalies in solution are inert, and a Monel woven filter-cloth is almost always used when strong alkali solutions have to be filtered, as in lime causticising. Such resistance to both acid and alkali indicates that the metal can be used for all normal salt solutions, unless these are strongly oxidising. Not only is this the case, but the copper of the alloy no longer causes stains and colours in the chemicals. A pure white table salt is almost always prepared in a Monel evaporator, while many photographic chemicals and dyestuffs are handled in Monel reaction vessels. In the preparation of ammonium sulphate by centrifuging a slurry of the salt with dilute sulphuric acid or dilute ammonia, Monel metal is always used for the centrifugal basket, as combining strength with corrosion resistance. Sulphide solutions are relatively inert, but the metal is not suitable for boiling sulphites and bisulphites.

In resisting the action of all forms of organic acids, the alloy behaves as a sort of super-copper, with corrosion rates much lower and less affected by aeration. For example, acetic acid, unaerated, never gives a figure of more than 30–40 mdd, whatever the strength or temperature, and an air-saturated 50% acetic solution will only attack at rates of 150 mdd. When organic and inorganic acids are combined, as in sulphation for the preparation of "soluble" oils, or in the sulphuric acid refining of petroleum, then Monel is very well suited to plant construction. The whole plant in such cases can be made from sheet or tube, and the very hard surface means that corrosion-erosion effects will be negligible. These can destroy the working surfaces of a mild-steel pump forcing hot coal tar to a pipe-still in a few days, but have no effect on Monel over continuous working periods of a year or more.

INCONEL *

This alloy, with the composition and mechanical properties set out in Table IX–5, has been designed primarily as a high-temperature acid-resisting metal. The original use was in a plant to hydrolyse fats under pressure at 300°, but the chromium content gives much better resistance *under oxidising conditions* than any one of the three alternatives: copper, nickel, or Monel. In reducing conditions it has no advantage over the last named, and is in fact rather more easily corroded either by acid or alkali.

TABLE IX–5

Composition (% by weight)	Ni 76, Fe 7·5, Cr 15·5, Cu 0·2, Si 0·25, Mn 0·25, C 0·1. (Usually defined as 76 Ni, 15 Cr, 8 Fe.)

Ultimate Tensile Strength (tons/sq. in.)	
Room temp.	39
200° C.	35
400° C.	36
500° C.	35·5
600° C.	34
700° C.	25·5
800° C.	14·3
900° C.	9·4

Brinell Hardness	135–260.
Izod Impact Value	70–120.
Thermal Conductivity	9 B.Th.U./sq. ft., etc.
Specific Gravity	8·51.

The mechanical properties of Inconel resemble those of Monel except for the greater strength at temperatures above 500° C. It can be machined, welded, and work-hardened in very much the same way as the latter, and castings can be made, though they are a little unusual.[8] The really striking feature of the alloy is the way in which strength is maintained at high temperatures. The 0·2% proof stress at 700° is 9·0 tons/sq. in., and long periods at even higher temperatures do not cause any changes in grain structure. Case-hardening boxes welded from Inconel sheet can be used in sulphur-free atmospheres up to 1150° C., without distinction between oxidising and reducing conditions.

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* Registered Trade Mark.

Corrosion Resistance

The chromium content confers resistance to a number of oxidising solutions which would attack Monel. For instance, nitrates, persulphates, and thiosulphates in solution have no action, and the alloy is particularly suited to the final manufacturing stages of certain photographic solutions in which metal contamination must be avoided. At the same time, a strongly oxidising acid salt, such as ferric or cupric chloride, will still give rise to high corrosion rates. Sodium sulphide has no action on Inconel, even in concentrated solution at boiling-point, and the metal is nearly as good as Monel for all concentrated alkalies.

Apart from these special conditions, the resistance at temperatures up to perhaps 300° for both acid and alkali is no better than Monel, but when fatty acids (stearic, oleic, etc.) have to be heated under pressure at temperatures of the order of 350°, Inconel is always used. It has the additional advantage that no attack by hot waste gas occurs, as shown by the fact that aircraft exhaust manifolds are normally made by pressing and welding the sheet metal. Immersion heaters for corrosive solutions can be sheathed in the tubing, which has also been recommended for pyrometer covers. Hot dry chlorine, fluorine, and the corresponding acid gases have little action up to 550°,[9] and oleum or liquid sulphur trioxide under pressure is equally innocuous.

NICKEL-CHROMIUM ALLOYS

The original use of these "nichromes", under all sorts of proprietary names, was in the manufacture of resistance elements, for electric heaters. This is still their principal use, but by virtue of the combination of nickel and chromium they are generally inert chemically, and retain this property to very high temperatures. A whole group having about the same proportion of chromium as Inconel, but with varying proportions of nickel and iron, will retain mechanical strength to 1000° and resist all normal furnace atmospheres. A strongly reducing waste gas containing much sulphur will call for an alloy containing more chromium, and the heat-resisting steels are to be preferred. A nichrome with more than

20% of chromium will tend to deposit a new crystalline phase on prolonged heating, with resulting brittleness.

The muffle furnace tube shown in Fig. IX–6 is made in Inconel, and can be combined with a conveyer belt of "Nimonic D" (Ni 37, Cr 18, Fe 45) to give a gas-tight continuous-furnace treatment for metallurgical work. Hydrogen is inert at all temperatures, while nitrogen does not form a stable nitride and hydrocarbon gases have only a feeble action, increasing with the iron content. On the other hand, rates of attack by sulphur dioxide rise sharply at temperatures above 800°, and H_2S is active as low as 400°.

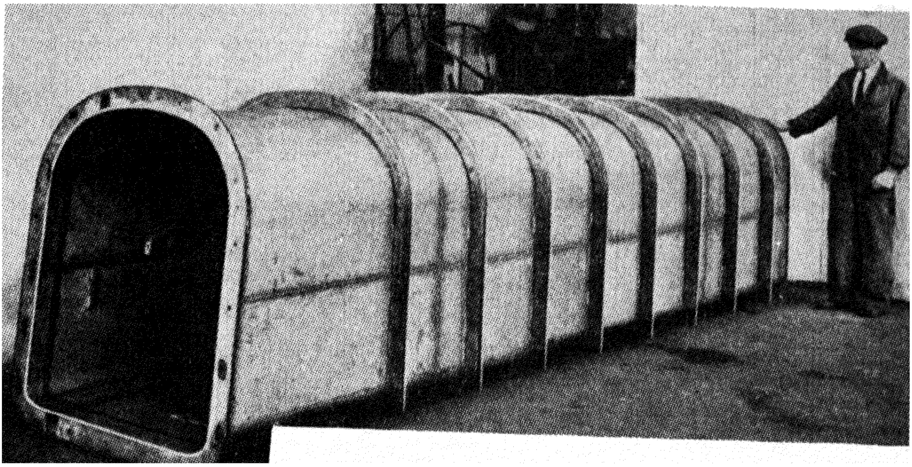

FIG. IX–6.—GAS-TIGHT WELDED INCONEL MUFFLE FOR WORKING AT 900° C. (*Courtesy of General Electric Co. and Henry Wiggin & Co., Ltd.*)

Although generally acid-resistant, the nichromes have not been much used for such plant as pumps or valves. Some proprietary alloys such as R.55 (Ni 53, Cr 23, Cu 5, Mo 4, W 2, Fe 8, Si 4) and Durimet (Ni 29, Cr 20, Cu 3, Mo 2, Si 1, and residual Fe) have been evolved for pumping strong sulphuric and hydrofluoric acids. For the latter they have obvious advantages over high-silicon iron, but they are still not suited for concentrated hydrochloric acid.

NICKEL-MOLYBDENUM ALLOYS

To achieve some resistance to this last reagent, it is necessary, as with the stainless steels, to incorporate molybdenum. The "Hastelloy", "Langalloy", and "Corrosist" proprietary alloys are of this type, as will be seen from Table IX–6. All these metals are sound constructional materials, with a strength of 20–35 tons/sq. in. and other properties reminiscent of a good cast iron. The effect of minor ingredients on all these properties is considerable, as suggested by Fig. IX–7.[10]

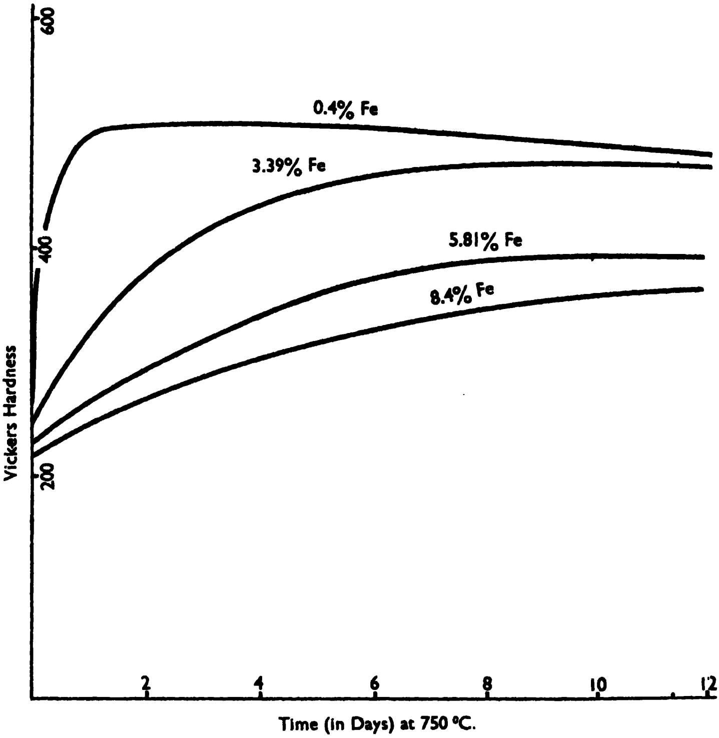

FIG. IX–7.—EFFECT OF IRON CONTENT ON CORROSIST HARDENING.
(After Hallett, *Proc. Chem. Eng. Grp.*, 1950)

TABLE IX–6. COMPOSITION OF CORROSION-RESISTING ALLOYS
(% by weight)

Name	Ni	Mo	Fe	Cr	Si	W	Cu	Mn	C
Corrosist B .	68	30	0·86		0·12				0·06
Corrosist C .	60	17	6·7	14·5	1·9				0·12
Corrosist D .	Nickel +				10·0				
Langalloy 4R .	63	30	5·0		0·75			0·75	
Langalloy 5R .	56	17	5·0	15·0	0·75	5		0·75	
Langalloy 6R .	85				10·0		3·0		
Hastelloy A .	60	20	20·0						0·10
Hastelloy B .	65	30	5·0						0·10
Hastelloy C .	59	17	5·0	14·0		5			0·10

It will be seen that there are three well-defined groups. Hastelloy B, Langalloy 4R, and Corrosist B are essentially the same, as are also Hastelloy C, Langalloy 5R, and Corrosist C. The silicon-bearing Corrosist D and Langalloy 6R represent an attempt at cheapening the alloy group, and have lost their resistance to hydrochloric acid to a large extent. All three groups are casting alloys, but a wrought form of Corrosist B, etc., known as Corronel B has recently been produced.[13]

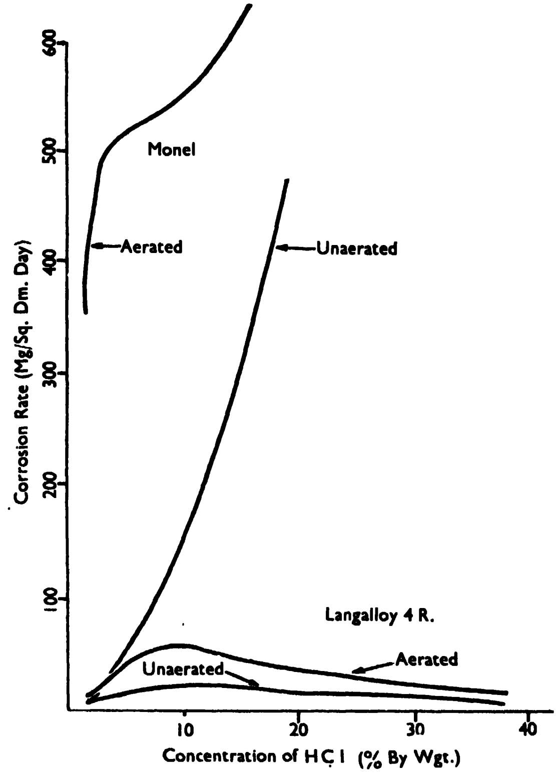

Fig. IX–8.—Attack of Cold Hydrochloric Acid on Monel and Langalloy.
(After Richardson, *Metallurgia*, 1949)

Just as Monel and Inconel can be described as types of super-copper, so these can be taken as an improved Monel. The outstanding advantage lies in resistance to hydrochloric acid, as shown in Fig. IX–8. A boiling 30% HCl solution only attacks Corrosist B (or its analogues) at rates of 400 mdd, and although this is high, conditions are very severe. Sulphuric acid has little action, even when concentrated and hot, as shown in Fig. IX–9, while phosphoric acid is equally inert. The chromium-bearing alloy group can be

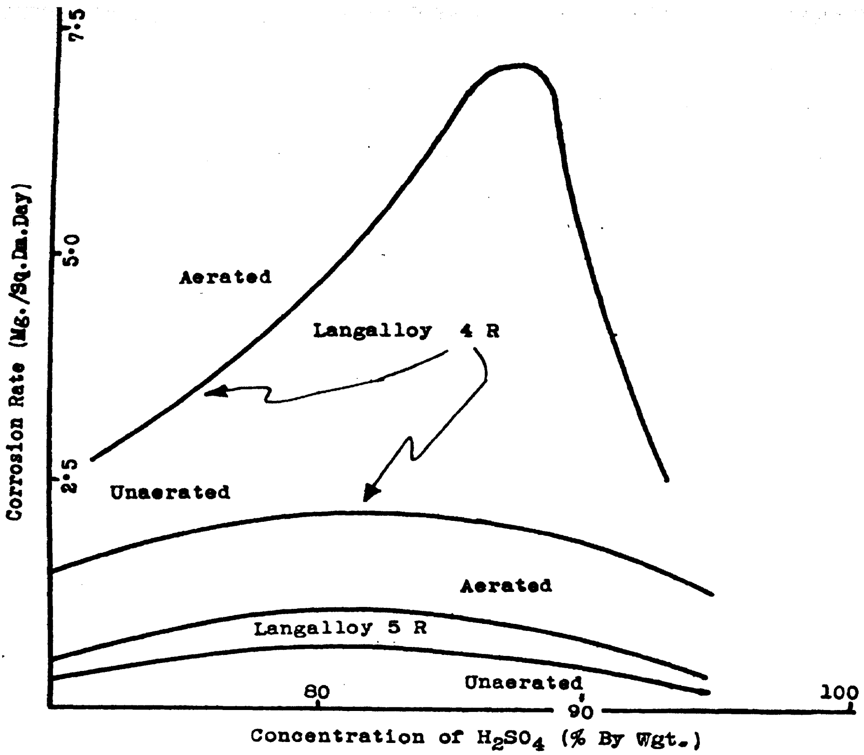

FIG. IX–9*a*.—RESISTANCE OF LANGALLOYS TO COLD SULPHURIC ACID.
(After Richardson, *Metallurgia*, 1949)

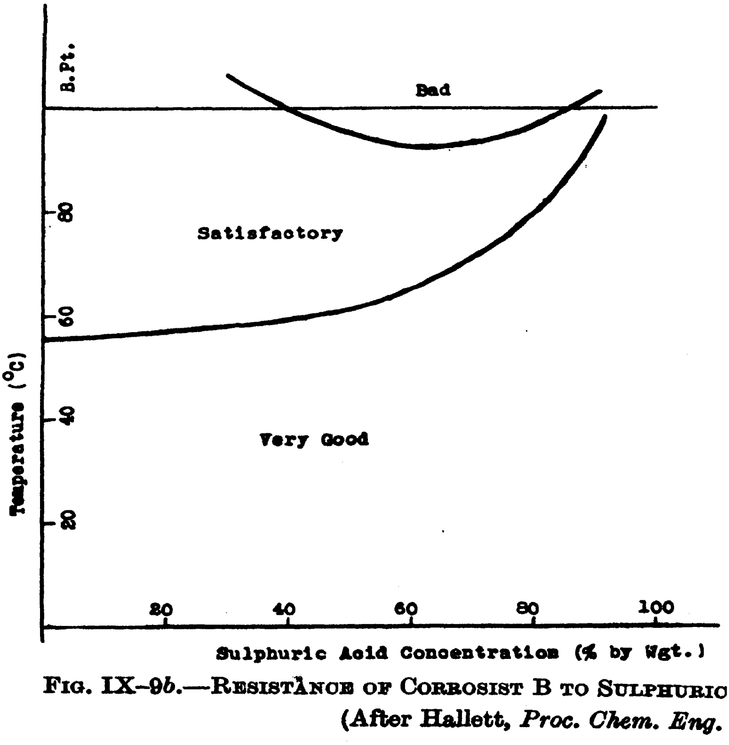

FIG. IX–9*b*.—RESISTANCE OF CORROSIST B TO SULPHURIC ACID.
(After Hallett, *Proc. Chem. Eng. Group*, 1950)

considered as a slight improvement on Inconel, as giving better resistance under oxidising conditions. They will resist even wet chlorine, iodine, and bromine, as well as oxidising salts in acid solution.[11] Silicon-bearing nickels such as Langalloy 6R seem to be a sounder metal from a mechanical standpoint than high-silicon iron. It is obvious that high cost will narrow the field of these very resistant metals to special purposes, but they appear to offer a very convenient reinforcement to non-metallic materials for such work as pumping and controlling very corrosive liquids.

REFERENCES

1. Morton, B. B., *J. Inst. Pet.*, 1948, 34, 1.
2. Bureau of Information on Nickel, "Nickel, etc., in Chemical Plant".
3. Henry Wiggin and Co., "Monel".
4. Colbeck, E. W., *Trans. Inst. Chem. Eng.*, 1949, **27**, 55.
5. Marshall, W. K., *Trans. Inst. Chem. Eng.*, 1944, **22**, 31.
6. Wachter, A., *et al.*, *Corrosion*, 1947, **3**, 406.
7. Henry Wiggin and Co., "Monel *v.* Sulphuric Acid", p. 7.
8. Henry Wiggin and Co., "Inconel".
9. Friend, W. Z., *Chem. Eng. Prog.*, 1948, **44**, 501.
10. Hallett, M. M., *Proc. Chem. Eng. Group*, 1950, **32**, 39.
11. Richardson, W. H., *Metallurgia*, 1949, **40**, 3 (see also *Nickel Bulletin*, Jan. 1950).
12. Friend., W. Z., and La Que, F. L., *Trans, Amer. Inst. Chem. Eng.*, 1946, **42**, 849.
13. Anon., *Ind. Chem.*, 1953, **29**, 397.
14. But see Mott, N. S., *Chem. Eng. Progr.*, 1952, **48**, 266.
15. Canzler, H., *Chem. Proc. Eng.*, 1952, **33**, 544.
16. Van der Hoven, H. W., *Chem. Eng.*, 1953, **60** (Aug.), p. 202.

CHAPTER X

HIGH-SILICON IRON

THE first effect of adding silicon to a normal iron is to convert the cementite present to graphite and ferrite. Cast iron containing more than about 3% of silicon will have very little combined carbon left. At the same time the temperature of the pearlite transformation (Chap. III) is raised considerably. An alloy with 6% of silicon is essentially a ferritic matrix with graphitic carbon inclusions, and the alteration in pearlite transformation gives a heat-resisting alloy —Silal—which has already been mentioned. This silicon content is not high enough to give any marked effect on corrosion resistance. As the amount is increased it approaches the limiting solubility of silicon in α iron, which is just on 15% at ordinary temperatures.[1] It is remarkable how rapidly the attack of many acids falls off as this limiting concentration is approached. A corrosion rate of 1000 mdd with 13·5% silicon in boiling 20% sulphuric acid drops to less than 50 as the content reaches 14·5. These rapid changes are illustrated in Fig. X–1, and are accompanied by a steady increase in hardness and brittleness.

The normal acid-resisting silicon iron, therefore, should contain at least 14% of silicon, and specifications[4] suggest from 14·25% to 15·25%. The carbon content is very important in determining the temperature of casting, and should ideally be adjusted to give with the silicon a minimum melting eutectic.[2] This calls for a range from 0·8% (14% Si) to 0·4% (16% Si). Other normal additions are manganese and phosphorus, which increase fluidity and reduce sulphur in the usual way, while a recent development has been the addition of 3–4% of molybdenum to increase resistance to hydrochloric acid. The silicon irons are sold under various trade names, and some of the most notable are set out in Table X–1.

These are all casting alloys, and the rough casting is hard, with a Brinell number of at least 450, and extremely brittle. The apparent tensile strength, measured by transverse rupture stress,[3] is from 6 to 15 tons/sq. in., but impact values are very low, and a ½-in.

TABLE X–1

Name	Composition (% by weight)						
	Si	C	P	Mn	Ni	Cu	S
Duriron . . .	14·75	0·85	0·12	0·66			0·025
Tantiron . . .	15·0	0·70	0·20	0·30			0·05
Ironac . . .	15·0	0·80	0·85	0·40	0·05	0·03	0·05
Thermisilid . .	15·5	0·55	0·13	0·57			0·02
Tantiron E . .	16·0	0·40					
Durichlor . . .	14·5	+ (3·5 — 4) Mo					
Le Creusot . .	15·2	0·6	0·08	0·90			
B.S. 1591 . . .	14·25 —15·25	0·35 —1·0	1·0	1·0			0·1

diameter rod can be snapped between the fingers. There is no possibility of tempering, and further shaping of the casting can only be carried out by grinding. Clearly the rough casting should be as near to final form as possible, a precaution which is made more difficult by the fact that solidification shrinkage is much more than for iron. Fresh castings are in fact in a marked state of strain and

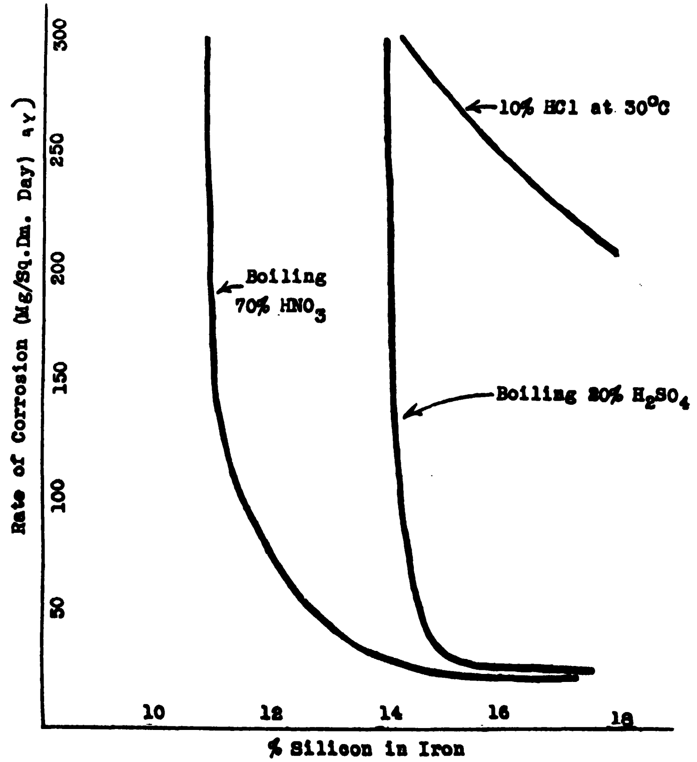

FIG. X–1.—ATTACK OF ACIDS ON SILICON-IRON ALLOYS.

must be stress-relieved by heating almost to softening-point. Specifications[4] usually call for a soaking period at 750°–850° for about four hours, followed by slow cooling. The stress-relieved casting is still apt to crack, and contracts have called for a period of service before final acceptance of the plant. The design of a casting should have these facts in mind. Large thin plates are very difficult to make, and sudden changes in section even more undesirable than with ordinary cast iron. Bolt holes must be replaced by slits, and any shape which calls for the use of chaplets or tie wires to support cores is not a practical proposition.

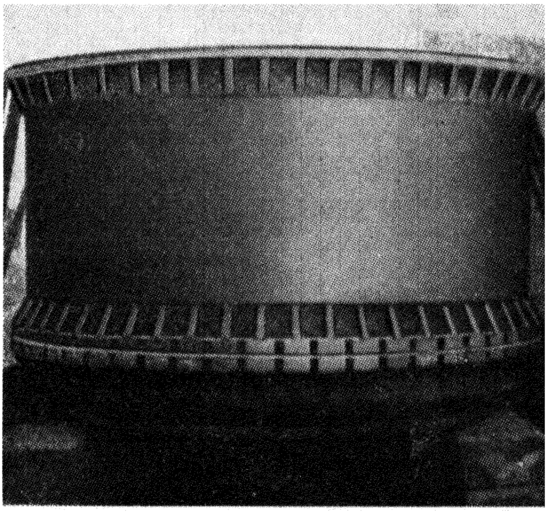

Fig. X–2.—Lower Section of HCN Generator in High-silicon Iron. Weight 2 tons.

(*Courtesy of Riley et al., Materials of Construction, Soc. Chem. Ind.*)

The metal can be welded, but only by heating the whole casting up to 700° and welding at this ambient temperature. Sections can then be gas-welded, with an oxidising flame and a silicon-iron rod; special fluxes are available from the British Oxygen Company or similar sources, but might in emergency be replaced by borax. Such a process cannot be an ordinary everyday affair on a chemical plant, and is probably reserved for the manufacturers. Very complicated forms can be avoided, and such operations as the closing of a tube to make a thermometer pocket become straightforward.

Castings in this material have in the past differed very widely in corrosion resistance, porosity, or even brittleness. This has been due in part to neglect of special precautions in casting, or to insufficient stress relief. Perfectly dry moulds must be used for the final process, while moisture and gases should be eliminated from the raw materials by a preliminary ingot casting. The temperature of pouring must be carefully controlled by an electric furnace and as much handling as possible carried out at above 700°.[2] The maximum weight of a finished casting will not normally exceed 1 ton, though Fig. X–2 shows that this is not an absolute ceiling. Although of recent years there has been a tendency to replace silicon-iron vessels by brick-lined steel, the metal still holds its place when high temperatures and high rates of heat flow are required. Serpentine condensers, with pipes up to 8 in. diameter and 10 ft. long, are often used in the condensation of nitric acid from denitration towers (sulphuric acid present), while steam-jet ejectors of the form shown in Fig. X–3 have been used for a variety of corrosive conditions.

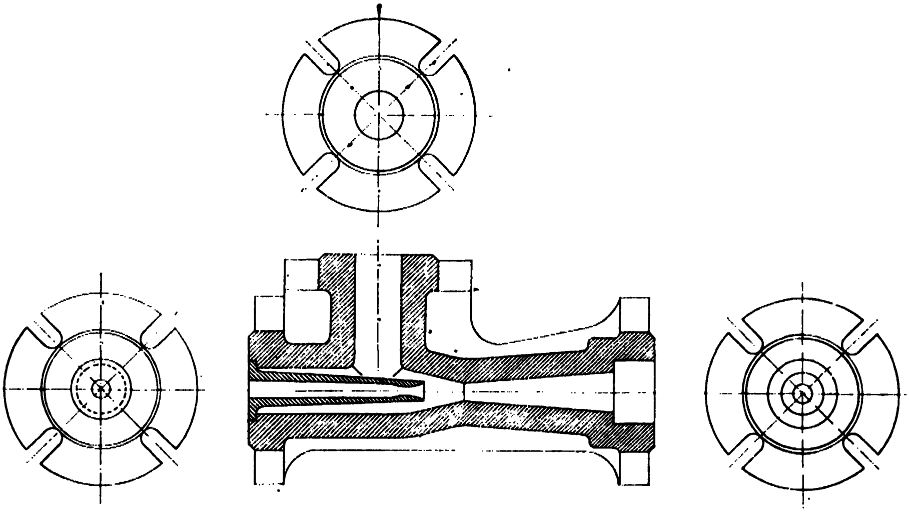

FIG. X–3.—SILICON-IRON EJECTOR.

(*Courtesy of John Varley & Co.*)

The thermal conductivity is somewhat lower than ordinary cast iron at 19 B.Th.U./sq. ft., etc., but is still much higher than that of stoneware at about 1. A wall of stoneware ½ in. thick will give a wall coefficient of 24 B.Th.U./(sq. ft.)(hr.)(° F.), while a similar thickness of silicon iron will have a corresponding figure of 455. When tubes of these dimensions are used for, e.g., condensing HNO_3, the fluid films might have joint values of 100, and the overall coefficients will be (*a*) stoneware, 19, and (*b*) silicon iron, 83 B.Th.U./(sq. ft.)(hr.)(°F.).

The difference in size for a given load will clearly be very striking. Reasonable conductivity also ensures that the metal will not fail by thermal shock, as does stoneware, and this makes its use in pumps for hot acid very common.

Corrosion Resistance

The sharp change in acid resistance indicated in Fig. X–1 suggests that resistance to corrosion is linked closely with the appearance of a second solid phase in the alloy. There is some doubt as to the exact mechanism, as the silicon appears to confer immunity from attack before it can be detected as a separate solid phase. Incidentally, as pointed out by Hurst,[2] more silicon is required to prevent atmospheric rusting than for checking acid corrosion. In certain circumstances, the surface of metal exposed to corrosion is covered over with a white film, which can easily be brushed off. It may be that this is some form of hydrated silica, which only covers the surface effectively when that surface contains a certain proportion of silicon. If this is so, then it would be expected that acid ions of great penetrative power, such as Cl^-, would tend to dislodge the protective membrane, while the larger ions will be inert. Hydrofluoric acid would react with the silica directly, and in fact crude phosphoric acid containing fluorides does attack the metal at much greater rates than a fluorine-free agent. Hydrochloric acid is far too corrosive for the ordinary alloys, but an increase in the silicon content to 17% does cut down attack to a very considerable extent.[5] The addition of molybdenum (Durichlor) provides a reinforcement to the silica film, perhaps of an oxy-chloride, which has much the same effect in reducing corrosion. Despite this reduction, the action of hydrochloric acid, except when dilute and cold, is still too high for commercial practice.

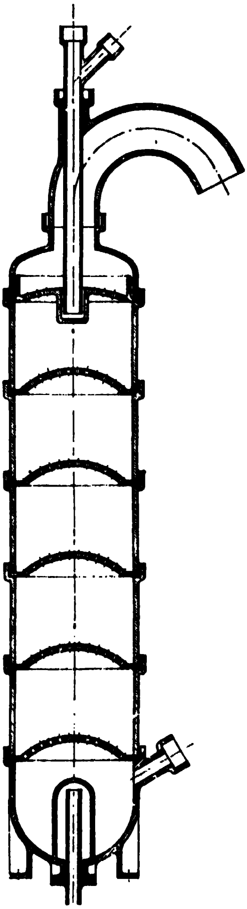

FIG. X–4.
(*Courtesy of John Varley & Co.*)

Sulphuric acid, in all strengths and at all temperatures, has practically no effect on proper silicon iron. The rate of attack is at its maximum with 20% H_2SO_4, but even here does not exceed about 25 mdd. The author has heard of less fortunate experiences with dilute acid, but it is probable that these have been due to the use of unsatisfactory alloys with a silicon content just below 14%. Directly-heated basins were used in a cascade concentration system for the manufacture of "water-white" acid with entire satisfaction. The process is disappearing in favour of oleum dilution, with silica or Pyrex equipment (Chapter 17), but shows the complete resistance given by the metal. Immersion heaters, generally used in vacuum concentrators of the Mantius type, are made from silicon iron with steam on the inside under pressure.[8] All forms of sulphuric acid concentration plant make extensive use of silicon iron, especially in positions where thermal shock is expected. The run-off pipes from Gaillard tower units, or from the older Kessler units,[6] were generally made up in this way, while the

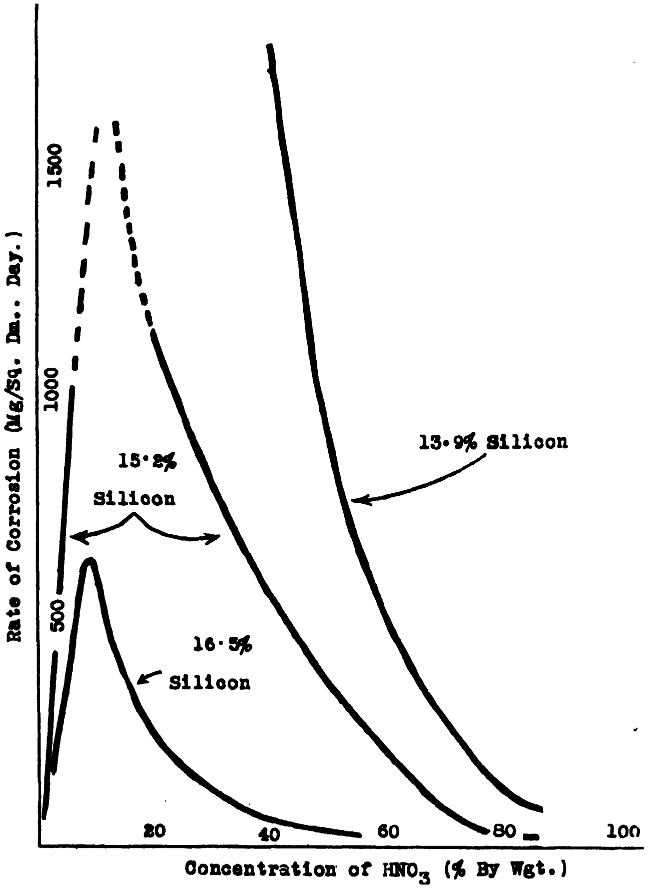

FIG. X–5.—CORROSION OF SILICON IRON BY BOILING NITRIC ACID.

whole of a denitration plant, with tower as shown in Fig. X–4 and a serpentine condenser, has been made in the alloy. This suggests that nitric acid is fully as inert as sulphuric, and the curves set out in Fig. X–5 are probably on the pessimistic side, though they again emphasise the importance of a silicon content. Oleum and free sulphur trioxide cause failure by cracking, while the evidence on sulphurous acid is conflicting.

Salts which may break down to form free HCl and HF, or are strongly oxidising in nature, such as sodium hypochlorite, can corrode, but only hot concentrated solutions attack at uncommercial rates. Resistance to other salts is complete, and many very unpleasant mixtures have been safely handled. Resistance in alkaline conditions is not nearly so good, and any caustic alkali in concentration above 30% will attack the metal rapidly. There is no reason, of course, why high-silicon iron should ever be used for these solutions.

As would be expected from its similarity to the Silals, the alloy is heat-resistant. A disastrous fire which destroyed an acid plant some years ago left the silicon-iron plant quite undamaged and apparently ready for service. It is also untouched by gaseous halogens, with the exception of fluorine, and only liquid bromine has any notable effect. The behaviour of this alloy resembles a metallic stoneware in almost every way, even to the point of needing a complex scaffolding support. It has two notable advantages in a much greater conductivity and a somewhat greater mechanical reliability, but is definitely much more expensive, and has, on the whole, lost ground in importance over the last twenty years.

An attempt[7] has been made to line steel vessels with silicon-iron places, using a very high-silicon alloy (70% Si) and soldering small sections into place with a lead-cadmium solder. This carries the analogy with stoneware still further, in that such a lined vessel looks just like a tile-lined plant, but gives higher thermal conductivity.

REFERENCES

1. Farquhar, M. C., *et al.*, *J. Iron Steel Inst.*, 1945, **152**, 457.
2. Hurst, J. E., *Trans. Inst. Chem. Eng.*, 1944, **22**, 72.
3. As in Cast Iron Tests (B.S. 321).
4. B.S. 1591 (1949).
5. Riley, R. V., *et al.*, "Materials of Construction", p. 118.
6. Parrish, P., and Snelling, F., "Sulphuric Acid Concentration (by hot gases)", Ernest Benn, 1924.
7. B.I.O.S. Report 1055.
8. Edgar, J. L., *Trans. Inst. Chem. Eng.*, 1952, **30**, 262.

CHAPTER XI

PRECIOUS METALS

It is proposed to deal under this heading with the "noble metals"—gold, silver, and the platinum group—and with tantalum and one or two other special metals that have recently been introduced into plant manufacture.

SILVER

This is the most important of the group, and would be widely used for chemical plant were it not for the cost of about 80*s*. per pound. The pure metal (about 99·99% Ag) has an ultimate tensile strength of 9 tons/sq. in., work-hardening to 20 tons. The annealing temperature is low (200°–300°) and the lower strength is the only one to be relied on. As the metal work-hardens, it passes from a Brinell hardness of 15 to one of about 100. The silver alloys used for coinage (in some countries) and for ornamental work contain up to 10% of copper and are much stronger. "Sterling" silver has 7·5% of copper and an ultimate tensile strength of nearly 20 tons/sq. in. before hardening. Such alloys are not used in chemical plant, for which the pure metal only is satisfactory.[1] The thermal conductivity of silver is higher than any other metal at 250 B.Th.U./sq. ft., etc., and the pure metal melts at 960° C.

The obvious use of silver is as a liner to stronger and/or cheaper metals, with some form of metallic bond so that the high thermal conductivity is utilised. Both steel and copper vessels may be lined with thin silver sheets in exactly the same way as for homogeneous lead lining. The clean metal is covered with silver-alloy solder, and heated to above the melting-point of this solder while pure silver sheets are rolled into position. The joints between the sheets are welded over with a silver welding rod and a slightly reducing flame. Molten silver dissolves oxygen, which is rejected on cooling to form cracks. For final elimination of flaws, the weld metal should be well hammered as with copper.

It is possible for a thin silver shape to be made the cathode in a copper-plating cell, and built up to a working thickness with the cheaper metal, but the process is uneconomic and unsatisfactory. The alternative electro-deposition of silver is open to the usual objection that the coating is porous, unless made very thick. In such circumstances, the homogeneous silver lining may be better and cheaper. "Silver-clad" steel or copper plates would be a desirable alternative, but do not appear to have been widely developed. A silver–copper combination would present difficulties welding, and the wide difference in physical properties makes hot-rolling of steel–silver layers a difficult problem. The clad steel can be welded, however, first by a steel weld, and then, after cleaning, by a silver weld on the other side.

Loose silver linings have been used, especially for autoclaves, where heat transfer may not be so important. Pressure equalisation of the space between lining and autoclave proper must be good. It is not sufficient to rely on a close fit, as pressure builds up in the small clearances, and the thin silver shell collapses inwards when the vessel is emptied. One of the advantages of the loose lining is that the silver can readily be recovered as scrap metal, with a bullion value of at least 70% of the total original cost. Some very large linings have been made in this way—Pirie[1] mentions one which was 30 ft. long and 2 ft. in diameter, with walls $\frac{3}{8}$ in. in thickness.

The normal all-silver plant is a great deal smaller, and has usually been employed for pharmaceutical chemicals in which a trace of metallic contamination is dangerous. Alternatively, many food products are discoloured by small quantities of copper, nickel, or iron—onions in vinegar which has been prepared in copper plant tend to assume a pale green colour.[2] It is easy to make solid-drawn silver pipe, and this avoids the welds which may be slightly anodic to annealed sheet. Condensers in silver have the advantage of rapid cooling and condensing when dealing with unstable organic vapours, and can be made in quite large sizes, as shown in Fig. XI–1. The metal is extremely ductile, and can be drawn out into very fine threads, as jewellers have known for thousands of years.

Corrosion Resistance

Silver is protected from acid attack by virtue of its high positive potential of +0·8 volts, which makes any hydrogen-liberating corrosion very unlikely. On the other hand, it does not form a stable oxide film, and a combination of oxidising conditions and a soluble salt will give rapid attack. The most typical instance is the ready dissolution of the metal in any nitric acid, but hot sulphuric acid behaves in the same way, evolving sulphur dioxide. Where reduction (of the acid) is difficult, as with acetic acid, silver may be extremely resistant and in fact can be used freely with any organic acid. Hydrochloric acid is a special case, in that the extreme insolubility of silver chloride may check further corrosion when once a complete film has been formed. Even this is dissolved away by hot concentrated hydrochloric acid, but is a very effective protection in

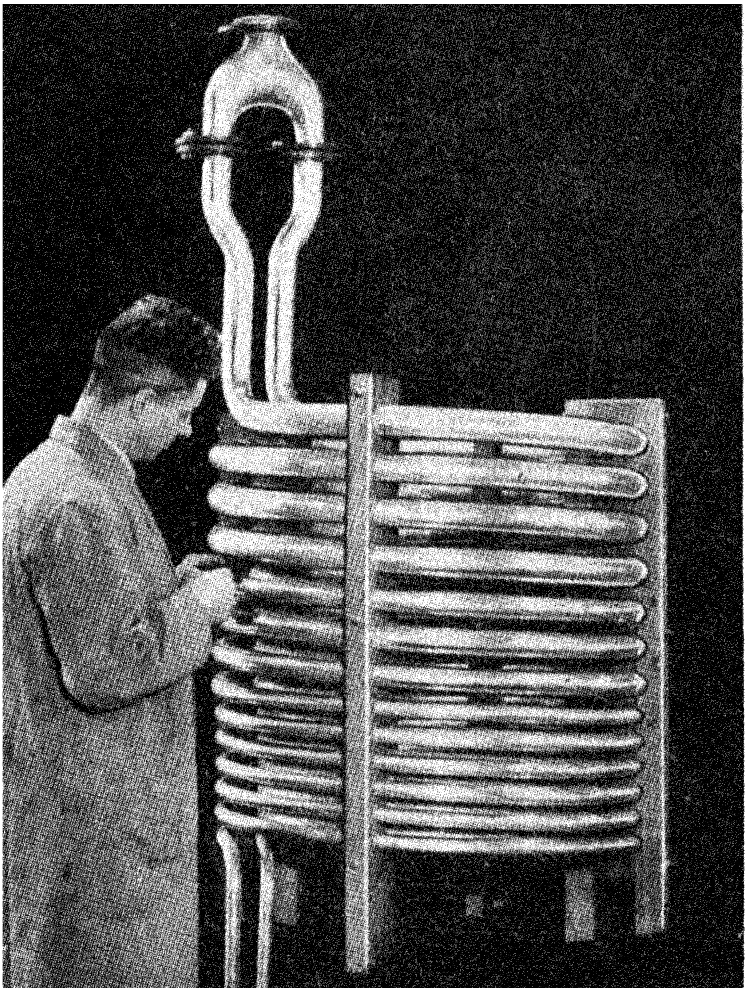

FIG. XI-1.—LARGE COOLING COIL IN PURE SILVER.
(*Courtesy of Johnson, Matthey & Co.*)

many circumstances, such as organic chlorinations. Similar protective films are formed with the other halogens and their acid solutions. Valves to control the flow of liquid bromine have all the essential parts made in pure silver, while brominations can be carried out in a silver-lined reaction vessel.

The extreme resistance to many organic acids is exemplified in the preparation of perfectly white phenol from a silver coil and condenser, or by the preparation of metal-free acetic anhydride. Acetate rayon solutions are extremely sensitive to metal stain, and for this reason silver valves and spinning jets are commonly used. As silver is completely non-toxic, it is an ideal material for use with all foodstuffs, though whether the cost will be justified is another matter.[3] A similar comment may be made on the very high resistance offered to caustic alkali, or to all neutral salt solutions.

Traces of hydrogen sulphide give rapid blackening of the metal at room temperatures. This is the cause of silver tarnish, which blackens all silver articles left exposed to normal industrial atmospheres. Moisture is necessary, as dry H_2S will not attack, and the film of Ag_2S, when complete, seems to check further action. The metal can easily be cleaned by cathodic reduction or rinsing in dilute nitric acid.

GOLD

The metal can only be used in very small parts or very thin coatings because of its cost, although in the old alchemical days gold basins were considered essential for handling hot sulphuric acid (vitriol). Gold in the pure state is too soft for practical purposes and is normally hardened with copper. The age-old assessment is the "carat", or proportion of gold present expressed in twenty-fourths. An 18-carat gold contains 75% of Au, with 25% of Cu, and such alloys are less resistant than the pure metal, as might be expected.

Apart from a high resistance to sulphuric acid and sulphur dioxide, it is difficult to find cases for the use of gold rather than silver in any form of chemical plant. An alloy with platinum or palladium has been used in the manufacture of rayon-spinning jets, as being harder and more inert than silver, and perhaps other uses of this kind may develop.

PLATINUM METALS

The metals of this group (Pt, Pd, Ir, Os, Rh, Ru) are, of course, almost completely inert to chemical reagents over a wide range of temperature. The pure metals are rather soft and mixtures are preferred, such as Pt–Ir (up to 10% Ir) or Pt–Rh (up to 10% Rh). These are excellent materials of construction, with the corrosion resistance increased, if anything, by the alloying addition. Palladium resembles platinum in most respects, and again is normally used as alloy with up to 10% of ruthenium or (for less corrosive conditions) 20% of copper. The other metals of the group are more difficult to work and hardly as resistant to general corrosion as platinum and its alloys.

The typical platinum alloy will have an ultimate tensile strength of 25 tons/sq. in. and a Brinell hardness which increases up to nearly 300. Machining qualities are good, while strength and rigidity are retained up to a very high temperature—at least 1400° C. Obviously such a metal could be widely used, were it not that a sheet 1 ft. square and ¼ in. thick would cost something of the order of £10,000 at the present time. It will only be in very special circumstances that the use of platinum can be contemplated.

One particular case is the handling of molten glass in the manufacture of glass wool or glass threads for weaving. Platinum jets, maintained continuously at a temperature of about 1400°, retain shape and size while the molten glass flows through to form fibres which are chilled in air or steam to solid threads. For special work, the furnaces are made entirely of platinum, thick-walled and heated direct by heavy electric currents. A trough some 12 in. long and 4 in. wide has the base perforated with 200 or more holes, from which the glass flows in threads of 0·02 mm. diameter, to be spun into threads by normal textile technique. Again, the preparation of peroxides by the electrolysis of acid solutions demands a very high anode current density. Any metal but platinum would be attacked very rapidly in these conditions, and the alloy lends itself readily to fusion into glass, followed by rubbing down to give a fine metal edge as the actual anode. Of course, the catalytic properties of platinum are unique, but often lead to use in very corrosive conditions. The normal synthesis of nitric oxides from ammonia, by reaction over platinum or platinum-rhodium gauze at 900°, means that the metal must resist both hot ammonia and nitric oxides, together with steam and air. This is hardly a use for plant construction, however.

It may be noted as an offset against the heavy initial cost that the rate of depreciation is negligible. In fact, under the working conditions of the last ten years or so, a heavy capital outlay in platinum may have represented, at any rate on paper, a very good investment. Platinum gauzes bought in 1939 could be sold in 1950 at considerably more than the initial cost.

TANTALUM

The development of powder metallurgy has brought this material into the scope of practical use. When once prepared in the form of thin sheets it can be shaped and welded, though only by very special techniques. Tantalum can be regarded as a flexible glass of high conductivity (36 B.Th.U./sq. ft., etc.), very considerable strength (26 tons/sq. in.), and high density (16·6). It exhibits very high resistance to all acids except hydrofluoric, and low resistance to all caustic alkalies.[4]

The only important use for this material so far determined has been in the absorption of gaseous hydrochloric acid in water. This entails the removal of considerable amounts of heat stored up in a very corrosive fluid, and has meant in the past a very clumsy absorption system. Now a much more compact plant can be built with tantalum walls, as shown in Fig. XI–2. The cooling surfaces could absorb heat at rates of over 100,000 B.Th.U./sq. ft. per hour and there was no attack whatever on the material, even when the HCl concentration rose above 35% in the solution. Resistance to boiling nitric acid of high concentration is quite as good, and the metal has perhaps better mechanical properties than aluminium at high steam temperatures. It is doubtful whether the high cost will suggest use in this latter case, while the introduction of plastic-bonded graphite (Chapter XIX) has limited development in the handling of hydrochloric acid. Resistance to hot concentrated sulphuric acid is poor, but if the temperature is reduced by vacuum, bayonet type tantalum heaters compare favourably with silicon iron.[5]

A tantalum lining for a steel vessel will cost less than a platinum cover, but is still costly—some £40 to £50 per square foot of a 0·02-in. sheet. Resistance to all the halides, wet or dry, is good, though there seems to be some doubt about fluorine. As stability to oxidising conditions is satisfactory, the metal may find a use as an electrode in the manufacture of peroxides, but it must be shielded from reducing conditions. Hydrogen can penetrate and embrittle tantalum rapidly, especially at high temperatures.

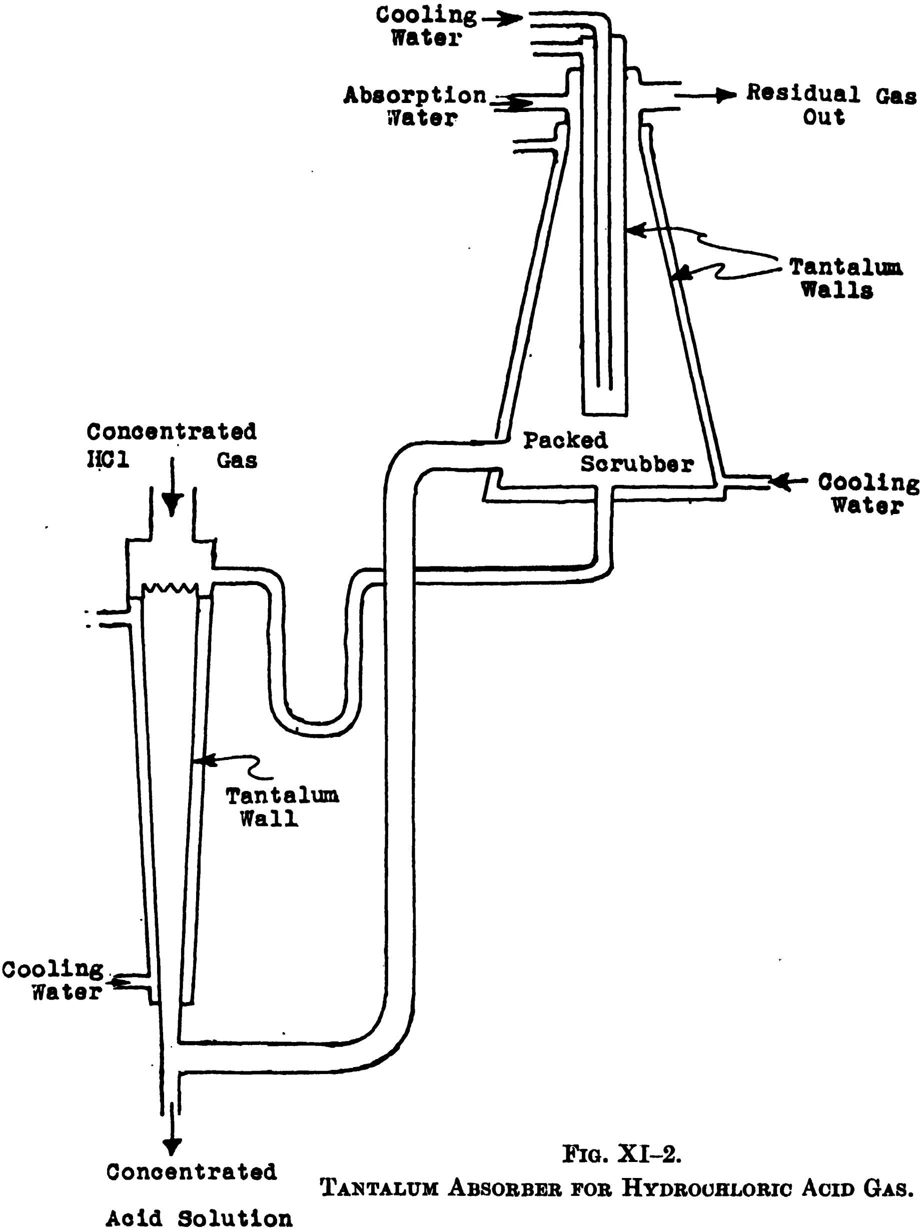
Cooling Water
Absorption Water
Residual Gas Out
Tantalum Walls
Concentrated HCl Gas
Packed Scrubber
Cooling Water
Tantalum Wall
Cooling Water
Concentrated Acid Solution

FIG. XI-2.
TANTALUM ABSORBER FOR HYDROCHLORIC ACID GAS.

ZIRCONIUM

This metal has only recently been made available in sheet or tube form. It is necessary to "hot-work" (above 1860°) a metal which reacts very readily with oxygen or nitrogen at all temperatures above 500°. The methods used involve hot-rolling in steel sheaths and will apparently call for very specialised techniques. The finished metal resembles mild steel in mechanical properties at ordinary temperatures, and will presumably retain very considerable strength when heated.

In corrosion resistance zirconium is definitely inferior to tantalum, being rapidly attacked by $HNO_3.HCl$ mixtures, and even corroded by hydrochloric acid alone. It is appreciably resistant to fused alkalies, and as good as tantalum in handling boiling nitric acid.[10, 12] One outstanding advantage over tantalum is in the lower specific gravity (6·5 as against 16·6), but the conductivity is much lower at 9·6 B.Th.U./sq. ft., etc.[7] It is doubtful if any chemical plant has yet been built which incorporates appreciable amounts of zirconium, but it may be of use in the future, especially in view of the relative abundance of zirconium ores in nature.

TITANIUM

In the search for lightness in engineering plant titanium alloys have repeatedly been tested, with interesting results. The pure metal has a specific gravity of 4·5, as compared to 7·9 for stainless steel, which it greatly resembles in mechanical properties though

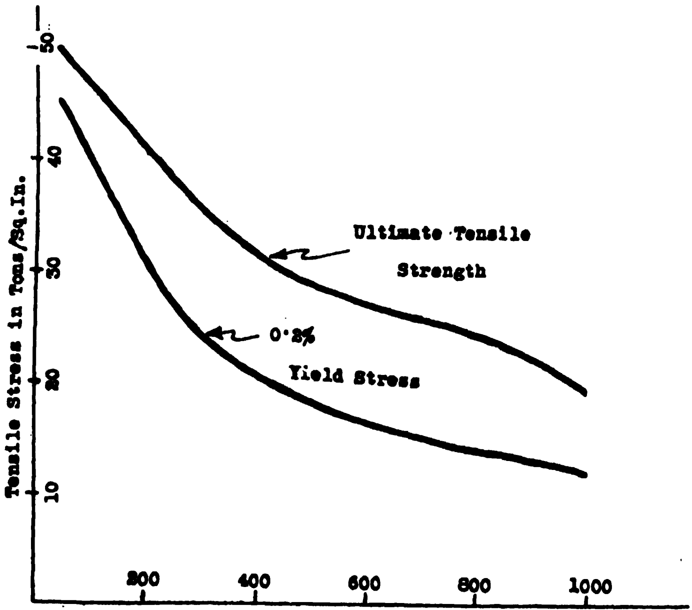

FIG. XI–3.—STRENGTH OF TITANIUM METAL.

(After Miller, *Ind. Chem.*, 1951, **27**, 483) more brittle, especially at low temperatures.[11] As will be seen from Fig. XI–3, mechanical strength is well maintained up to 800°, and combined with a resistance to oxidation and scaling fully equal to the nickel-chrome steels. The metal cost about 40*s*. per pound in 1951, but it was hoped to cut this cost very much by improved methods of production in the following five years.[6, 8]

It was originally claimed that corrosion resistance was as good as that of stainless steel, but it is now generally recognised as somewhat inferior. Resistance to HNO_3 is good but far from absolute, while the rate of attack of sulphuric acid and hydrochloric acids is definitely too fast for normal use. On the other hand, aerated salt solutions such as sea water have practically no action.[13]

A number of titanium alloys have been investigated, but none have so far found wide application.[8]

MOLYBDENUM

In the form of an alloying constituent, this metal has conferred HCl-resistant properties on steel and nickel, but used alone it is not particularly stable. Other acid solutions, with the unusual exception of hydrofluoric acid, will also attack at fairly high rates, and the metal does not therefore appear to be of any great interest.

A number of other metals, of which the most important is tin, are only known in chemical plant in the form of coverings for a less expensive or more reliable supporting material. They will be dealt with in the next chapter.

REFERENCES

1. Pirie, J. M., "Materials of Construction", p. 181.
2. McDonald, *Proc. Chem. Eng. Group*, 1931, **13**, 50.
3. Butts, A., and Giacobbe, J., *Chem. Met. Eng.*, 1941 (Dec.), p. 76.
4. Taylor, D. F., *Ind. Eng. Chem.*, 1950, **42**, 639.
5. Edgar, J. L., *Trans. Inst. Chem. Eng.*, 1952, **30**, 262.
6. Titanium Symposium, *Ind. Eng. Chem.*, 1950, **42**, 214.
7. Miller, G. L., "Zirconium", *Murex Review*, 1951.
8. Miller, G. L., *Industrial Chemist*, 1953, **29**, 102, 207.
9. Anon., *Chem. Eng.*, 1953, **60** (April), 105.
10. *Ibid.*, 1953 (Sept.), 304.
11. Tyler, W. W., *et al.*, *J. Metals*, 1953, 5 (Sect. I.), 1104.
12. Miller, G. L., *Industrial Chemist*, 1953, **29**, 482.
13. Harple, W. W., *et al.*, *Chem. Eng, Progr.*, 1953, **49**, 566.

CHAPTER XII

PROTECTIVE COATINGS ON METALS

THESE protective coatings have been evolved for iron and steel and are rarely used for any other metal. There is little purpose in coating further an expensive material which has been chosen because of its own inherent corrosion resistance. Certain coverings, applied as sheets and retaining their own characteristics (e.g. homogeneous lead lining), have been or will be considered elsewhere. Only such coatings as are put on by brushing, spraying, dipping, electroplating or heat treatment are dealt with below. The line of demarcation is admittedly indistinct, but these latter processes tend to produce a more porous and less satisfactory coating than the more expensive sheet lining.

GALVANISING

This is the most important and firmly established form of protection for ferrous metal. The process is simple, the cleaned iron section being immersed in molten zinc at a temperature of about 500°. The metal has previously been cleaned from scale by acid baths and dried in air; a trace of oxide is left, which a thin layer of molten chlorides on top of the zinc removes before the clean iron and zinc come into contact. Dipping temperatures are high enough for the metals to form an alloy, which shades out from iron-rich zinc to a pure zinc metal at the surface. The thickness of this alloy layer will vary from 0·0004 to 0·005 in., and attachment to the metal below is very good. It is seldom that a galvanising layer lifts from the iron, as distinct from painting or electroplating. The main disadvantage of the hot dip is that a complicated section may be distorted by the heat. Costs of galvanising vary widely, but can hardly be less than two to three times the value of the zinc used. A layer of the metal 0·001 in. in thickness will weigh 3·6 lb./100 sq. ft., which with zinc at 1*s*. 3*d*. per pound (Sept. 1952) costs 4*s*. 6*d*. The cost of covering 100 sq. ft. of plate will be at least 10*s*.–15*s*. on this basis, but it is difficult to quote any real general figure.

The great advantage of galvanising over other forms of metallic coating is that the zinc is anodic to iron in all normal corrosive conditions. A scratch or abrasion may expose the underlying metal, but this forms a cathodic area, while the anodic zinc surround merely corrodes a trifle faster. It is protected itself, in all neutral or nearly neutral conditions, by the formations of an oxide skin, more or less hydrated.[1] This skin only persists over a relatively narrow *p*H range, as shown in Fig. XII–1. The film of hydrated oxide formed at ordinary temperatures is gelatinous, and shrinks on heating, so that more corrosion occurs, a maximum rate being noted at 60°–70° (Fig. XII–2). As heating proceeds, the film hardens and extends to cover the surface completely, so that the corrosion rate falls again. It is possible that the electrochemical character of the two metals may alter with temperature.

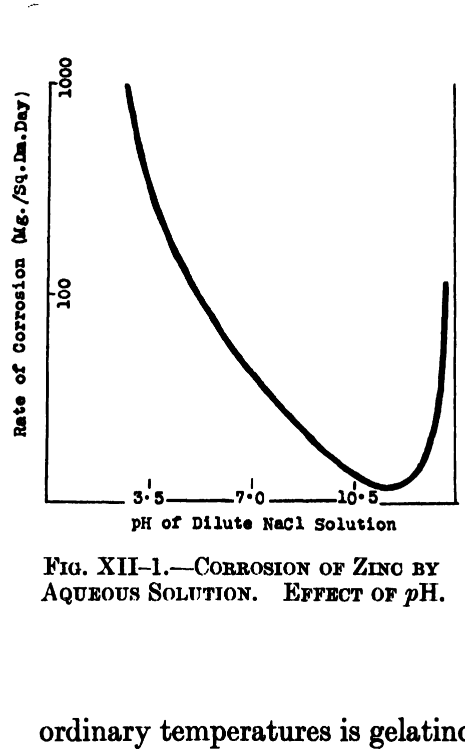

FIG. XII–1.—CORROSION OF ZINC BY AQUEOUS SOLUTION. EFFECT OF *p*H.

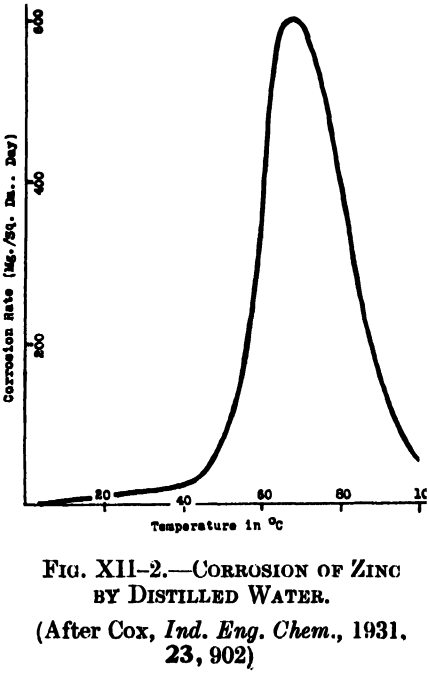

FIG. XII–2.—CORROSION OF ZINC BY DISTILLED WATER.

(After Cox, *Ind. Eng. Chem.*, 1931, **23**, 902)

When a galvanised surface has once "weathered" in this way, corrosion in solutions of *p*H 7–11 is very slight. Galvanised iron tanks have been used for fifteen years and more in the handling of (sodium chloride–calcium chloride) solutions with no sign of pitting or failure of the coating. Although the inertness of zinc (normal electrode potential —0·762 volt) must be due in great part to the formation of an oxide skin, the presence of oxygen increases corrosion rates slightly, so that some cathodic check on attack exists. A very soft water will give more rapid attack on metallic zinc (20 mdd) than a 10% solution of sodium chloride (5 mdd) and ordinary hard water has no measurable action. Refrigerator brines (concentrated solutions of NaCl, $NaNO_3$, and $CaCl_2$), with a *p*H adjusted to the range 8–10, are pumped through galvanised steel pipes and stored in galvanised tanks, thus avoiding the rust precipitates which an unprotected iron surface would cause. It must be noted that *hot* concentrated salt solutions can cause severe pitting, perhaps because of the partial breakdown of hydroxide film mentioned above. The pitting can go on even when fair concentrations of chromate (up to 4 gm./litre) are present.[2]

A galvanised iron surface exposed to atmospheric attack will have a life proportional to the amount of zinc that has been applied.[3] The rate of attack is about 1 mdd, and although the coating is usually thin a life of the order of ten years can be expected.[16] It is generally the case that the corrosion is uneven, and pits will form, probably by uneven aeration, as Evans and Davies[4] have shown for zinc immersed in water.

As far as chemical plant is concerned, only in almost neutral conditions is galvanising an effective protection. The zinc is much more reactive than iron in basic solutions, and at least as active in acid conditions. Galvanised pipes laid in acid soils corrode as rapidly as the bare iron pipe. In a neutral soil, without drainage of industrial waters, a galvanised pipe may last longer, but the saving is doubtful. Sacrificial zinc anodes have already been discussed in Chapters I and III, but apart from this the protection afforded by galvanising is negligible in really corrosive conditions.

A mixture of cadmium and zinc has sometimes been used for hot-dipping, with some improvement in resistance to alkaline conditions, but the cathodic effect of the zinc is reduced. Electroplating can be used for covering steel with zinc, but the coating is much more porous than that given by dipping, and the method is only suitable for protection from atmospheric corrosion. In a typical case, the production of metal window-frames, coverings of zinc applied electrically were further protected with phosphate solution before a final painting.

TIN-PLATING

This process is normally carried out in the same way as in galvanising, with cleaned iron dipping into a bath of molten tin. In view of the expense, tin coverings rarely exceed 0·001 in. in thickness, many commercial plates only carrying 0·00002 in. Such lightly coated plates have been made for food canning, and are suitable for this because in weakly acid solution the tin is feebly anodic to iron and very inert to corrosion. Tin-plated surfaces for severe conditions must carry at least 0·001 in. of plating, equivalent to some 4 lb./100 sq. ft. The actual cost of dipping will not be more than for galvanising, but the metal cost is much higher. The price of tin has fluctuated widely over the last few years, reaching a maximum of £1100 per ton in 1951. It follows that the cost of the metal will be about £2 per 100 sq. ft., but this may not be very heavy for the comparatively small areas of a piece of chemical plant. Tin coatings which have been deposited electrolytically are porous and normally to be avoided.

A tin surface is not definitely anodic to iron, and will often accelerate rusting at pinholes. It is the more essential that covering be complete, which means a heavy coating. A pure tin surface has a very low solution potential (—0·136 volt) and hydrogen overvoltage effects will stop acid attack in reducing conditions. Firm oxide layers do not form easily, however, and dilute unaerated HCl or H_2SO_4 will corrode at rates of the order of 50 mdd. This is about the same as for copper, but the salts, instead of being strongly coloured, are quite colourless and non-staining. As tin is non-toxic it is used freely in all foodstuff manufacture where acidity may develop.[5] Tin-lined copper plant, heating or cooling milk, has the advantage of high conductivity, while corrosion does not show in colour or taste. Even when the attack has proceeded so far that copper is exposed, it will be cathodic to the tin and only very slowly affected. Caustic alkalies attack tin, so that the lined plant cannot be cleaned with strong alkaline detergents.

The action of very soft water is very slight, and the preparation of "conductivity" water usually entails a tin-lined copper condenser. Distilled water saturated with carbon dioxide can pick up more than 10 parts per million of metal from a copper condenser in a normal distillation process, but a very light coating of tin can reduce this to less than 2 ppm. This illustrates the fact that the principal use of tin-plate in chemical plant is to prevent staining and contamination rather than to check plant corrosion. It is, however, definitely more inert than a zinc-covered sheet in acid conditions, and especially valuable for all food-product handling. A very comprehensive account of the corrosion resistance of tin has recently been published.[6]

LEAD-COVERED PLATE—TERNE-PLATE

Pure lead does not wet iron or steel, so an alloy containing up to 25% of tin is used, the process following the normal lines of hot-dipping. No great resistance is offered to corrosive conditions, as the coating appears to be more porous than either zinc or tin alone. Adhesion is not good, and a preliminary coating of copper has sometimes been used. When the lead-alloy sheath is broken by cuts or scratches the iron is anodic and rapid rusting ensues—at least in acid conditions. Polarity is reversed in alkaline solutions, but the iron would not be attacked in any case. In these circumstances it would not appear that the lead-covered sheet is made by hot-dipping will be of much interest for chemical plant. The cheaper cost that once characterised Terne-plate as against galvanised iron is disappearing with the soaring cost of lead.

ELECTROPLATING

The coverings put on by any such process are porous until a thickness of at least 0·001 in. is reached, and for any given thickness are less satisfactory than the hot-dipped film. This means that considerably heavier coatings must be put on for chemical plant than in ornamental metalwork. It is possible to deposit metal on any conducting material, but the adhesion of the film to the underlying surface can be very bad. Complicated shapes are not easily plated to an even depth, and weak places lead to a stripping of the entire film. As a result, when a metal can be applied to steel by hot-dipping, electroplating is seldom used—at any rate in strongly corrosive conditions.

Chromium is normally deposited electrolytically and even then needs a preliminary coating of copper and/or nickel. Were it possible to obtain a perfect coating on mild steel, this might be a rival to stainless steel. Unfortunately the coatings are brittle, and any crack means an anodic area and intense pitting. In fact, the only use for chromium plating is in protection of surfaces from erosion, and no reliance is placed on these films for real corrosion resistance.

Nickel, cadmium, and silver platings are more satisfactory from the point of view of adhesion, but are still porous. Attack through the pores is almost certain to lift the adjacent film and all trace of protection soon disappears.

METAL-SPRAYING

This process involves feeding metal powder or metal wire into a hot-gas blowpipe (Schori pistol), which melts the material and conveys it in molten form to the surface to be covered. Theoretically any metal of melting-point below 1600° can be sprayed,[7] but in practice only lead, tin, zinc, and aluminium are of any real importance though nickel has been used successfully. The great advantage of this process over hot-dipping or electroplating is that it can be applied directly to large plant sections *in situ.* Coverings are irregular, but can be made much heavier at any special points of incipient corrosion. It is not possible to spray the inside of pipes unless the spraying gun can actually be taken in, but the process is an excellent way of covering large steel frameworks exposed to the atmosphere of a chemical plant. Naturally the iron surface must be cleaned, preferably by sand or shot blasting, before being covered by metal spray. Each pass of the gun puts on about 0·003 in. of zinc or lead—a much heavier coating than can conveniently be applied by electroplating and almost as much as the heaviest galvanising. Information is not available as to chemical resistance, but the method certainly gives very good protection against sea-water corrosion. Sprayed aluminium gives a very durable finish to exposed steelwork.

"METALLISING" FINISHES

By special treatment it is possible to confer on a steel surface some of the characteristics of aluminium, chromium, or silicon. The section to be treated, usually of comparatively small size, is packed in a container with suitable reactants and heated. Length of treatment varies with the depth of penetration required, and the method may be regarded as a substitute for the "hot dip", in which high-melting metals may be used, and the same alloy structure obtained.

Sheradising deposits zinc on the surface, and is used for small parts, such as bolts and nuts, instead of the normal galvanising. They are simply heated to 350° in a container packed with zinc dust and a very even coating is obtained, with no distortion. As the covering is usually very thin, the process will hardly be used except to withstand ordinary atmospheric corrosion.

Calorising is designed to form a skin of aluminium, and the heating must be carried out at 900°, with a mixture of metal powder and chloride. A calorised steel has remarkable heat resistance, in that it can be heated to 750° in air with no appreciable change; ordinary mild steel will gain up to 10% in weight in 24 hours by oxide formation. No doubt the characteristic aluminium oxide skin is formed and further attack is inhibited. The treated surface is very resistant to SO_2–SO_3 mixtures and can be used in building heat interchangers in contact plant. Unfortunately, protection does not extend to the normal aqueous corrosive agents, and dilute nitric acid will attack almost as rapidly as with ordinary steel.

Chromising is carried out at 1000°–1200°, with ferrochrome powder, aluminium, kaolin, and ammonium fluoride. The reaction is complex, but a chromium alloy gradually forms on the steel surface. A layer containing about 13% of chromium will be formed in 3 hours at 1000°, and gives effectively a stainless iron cover for the mild-steel plate. As the normal layer thickness is only about 0·005–0·01 in., the amount of chromium is much less than even in "clad" plate, but the protection seems to be quite adequate while it lasts. The potentialities of an anodic area being formed are such as to preclude use of the process except in mildly corrosive conditions.

Siliconising, by heating at 1000° in ferro-silicon powder, with a chlorine atmosphere, puts a thin layer of high-silicon iron on the ferrous surface. Clearly it is subject to the same disadvantages as the chromised surface. Nobody would be prepared to take the risk of exposing such material to very severe conditions for fear of a sudden attack and penetration. Both processes, however, give to small parts a very considerable increase in surface hardness, while leaving the core ductility and strength unaffected, and are of great interest in case-hardening for all sorts of mechanisms.

INORGANIC COATINGS

Nitriding is a form of case-hardening which might find application in pump or valve parts, but as with the methods above, is mainly of interest in more complicated machines. The steel parts are heated to 500° in ammonia and a surface nitride is formed. It is extremely hard, Brinell figures up to 1100 having been recorded, and resistant to atmospheric corrosion up to 500°. Chemical resistance apart from this is not remarkable.

A number of inhibitive treatments for steel have been based on the sparingly soluble layer of *ferrous phosphate* which is formed on treatment with dilute phosphoric acid. It is usual to remove scale from iron sheet before painting, and similar processes by immersion in dilute sulphuric acid, followed by a water rinse. If the plate is now given a hot dip of 3 minutes in 2% phosphoric acid, or a mixture of manganese and iron phosphates, a firm layer of crystalline phosphate is formed, which is remarkably adherent. The residual acid can be washed off, or left to dry on, and the sheet treated in this way will resist attack by wind and weather for several months without developing rust spots. This is a valuable property when complete continuity in a painting process cannot be ensured. The layer is an extremely good base for paints or enamels, and also forms an absorptive agent for mineral oils. Phosphating, followed by enamelling, is an alternative to tin-plating for food storage vessels, and small metal parts are very easily protected from rust formation by the same acid treatment followed by oiling with linseed oil–paraffin mixtures. Mixtures of phosphoric acid with wetting agents and grease solvents are commonly used for cleaning rusty metal parts, and leave them in a state fit for immediate painting. All these processes have been carried out under various proprietary names (Parkerising, Bonderising, Jenolising, and so on.). For chemical plant it is probable that the main use of phosphate coatings lies in preparation for painting, as suggested below.[18]

Chromate protection, as distinct from phosphating, seldom puts on a definite film. A 20% solution of $CaCl_2$, containing 1% of sodium chromate, has practically no action on steel, but if the solution is subsequently replaced by one containing no chromate the metal begins to rust almost at once. For this reason it has been suggested that the principal function of chromates in checking steel corrosion is the oxidation of ferrous ions to ferric—the resulting deposits having better covering power.[8, 9] On the other hand, chromate solutions give much more permanent effects with zinc (galvanised iron), tin, and aluminium. In this last case chromate treatment of aluminium is an alternative to anodising, and the action with these metals may be through oxide formation, with parallel reduction to a chromium chromate. Whatever the mechanism, it is not so effective with iron, and the most permanent effects with this metal are obtained by including the chromate in paints—usually as a zinc chromate.

ORGANIC FILMS

Paint is the almost universal protection against atmospheric attack, especially with iron. It is essentially an elastic covering which hardens slowly, either by heating (stoving enamel), evaporation (solvent removal from heavier oil), or "drying" (oxidation and polymerisation of drying oils). In all cases a film of inert material is supposed to cut off contact with the corrosive medium. In actual practice a non-porous coating is very hard to obtain, and attack through pinholes or cracks spreads over the entire surface. Exposure of metal through a crack often develops an electrochemical couple in which the paint surface is cathodic to the plain metal.[10] Then solution occurs at the crack, and re-deposition as hydroxide under ordinary aerated conditions will tend to lift the paint edges. A characteristic upthrust of rust cones follows, with attack apparently taking place from below. Fig. XII-3 shows a typical case of paint breakdown. If paint has been applied to a steel surface which contains, indiscriminately, areas of ferrous and ferric oxide, moisture, and traces of salts, adhesion of paint is poor and electrical forces large, so that corrosion proceeds apace. On the other hand, if the metal surface has been cleaned, dried, and rendered homogeneous by some form of chemical treatment, adhesion is good and the local electrical effects less marked.

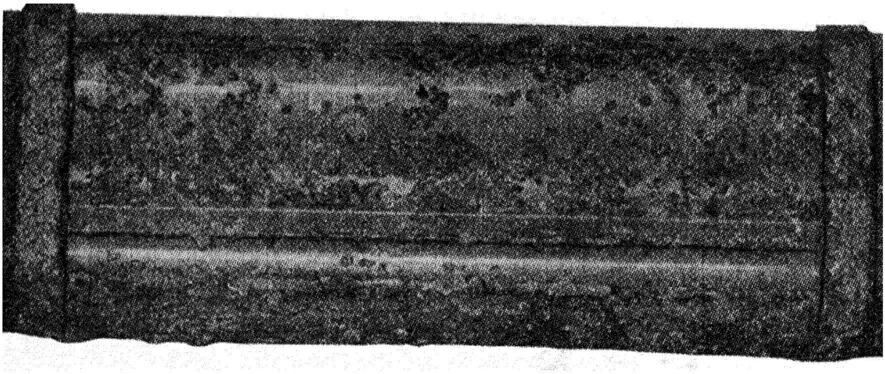

Fig. XII-3.—Paint Failure after 18 Months. Wire-brushing followed by One Coat Red Lead and Two Coats A.R. Paint. Industrial Atmospheric Conditions.

It is essential, therefore, that the metal surface be properly prepared before painting. In a case known to the author, wire-brushing of a steel surface before painting gave the subsequent paint film a life of three months (acid fumes in a marine atmosphere). When the wire-brushing was replaced by grit-blasting, the film lasted twelve months, while flame-cleaning or phosphating gave the same paint a life of over two years. (Flame-cleaning is a heating process in which an oxy-acetylene flame plays over the steel surface, cracking off dense scale and forming an even oxide layer.) Even with these precautions the paint film is never really continuous in the sense that corrosive agents cannot reach the metal below. Moisture and other vapours can diffuse through, while traces of dust, hairs, and pinholes can always be found. The best paints for corrosive resistance contain protective elements, such as zinc or lead, which can confer some additional form of protection on the metal below.

Red lead appears to function as an anodic inhibitor at points where the paint film breaks down. The effect is only notable in neutral conditions, or with natural waters of low salt content, and may be due to adsorption of lead compounds at the anodic surfaces.[11] Zinc can be incorporated into any paint mixture, to function as a sacrificial anode, but the amounts required appear to be greater than can be conveniently used. Zinc chromate is more effective, and will give a steady low concentration of CrO''_4 ions in any normally corrosive conditions. Aluminium metal can easily be obtained in the form of flakes, which cover a much greater area than grains and mask the metal surface below. The very stable film of aluminium oxide prevents any notable sacrificial action with regard to iron, but perhaps some slight cathodic protection is obtained. Iron oxide, in certain forms, has the same flake characteristics and some of the protective power of aluminium.

The carrying vessel, forming the adhesive film in which these inhibiting agents are suspended, will commonly be a drying oil, of which linseed is the most typical. It should be as waterproof as possible, and good protective painting on iron calls for two coats (at least).[15] The inner will carry the corrosion inhibitor, while the outer should be designed to repel moisture. As a typical example, the first coat on exposed steelwork should be a red-lead oil paint, and this can be followed by casing layers of drying oil carrying iron oxide flakes. Linseed oil is generally combined with tung and other vegetable oils, or replaced completely by synthetic resin paints, although in this country linseed oil combined with lead or zinc chromates gives the most effective protection to exposed steelwork.[12]

Bitumen- or tar-based paints are not quite so good for ordinary atmospheric protection as the drying-oil mixtures, and are much more susceptible to temperature change and oxidation. A hot tar spray on to clean steel will show a network of cracks after a few weeks, while thick layers soften badly and tend to run down in unsightly fashion. Part of this is due to the very good absorption of heat radiation, and this factor makes temperature control of tar-painted tanks difficult. Despite these disadvantages, a simple tar or bitumen paint, often applied as a hot spray, is the cheapest form of protection for large areas of metal. A typical example is found in the treatment of large gas-holders, as used in the distribution of gas fuel ("gasometers"). These have been tar-sprayed, normally after an initial priming coat of red lead, and the spraying renewed at intervals of about five years. Despite constant wetting by rain and immersion (water-sealed types) many very large holders have been in use for over fifty years, with the original steel plates of $\frac{1}{8}$ to $\frac{1}{4}$ in. thickness maintained in excellent condition. The inside surfaces are exposed to strongly reducing gases (containing up to 50% of free hydrogen and less than 0·4% of oxygen) and appear to need no protection. Of late years lime and rubber have been added to the ordinary crude tar, or to selected tar fractions, and such paints are more resistant to chemical attack than the reactive drying oils. A carefully selected bitumen (not tar from coal) will be almost inert to cold hydrochloric acid, and containers can be *improvised* by painting steel tanks with such mixtures. The process is not recommended for permanent plant, and in general no paint will give satisfactory service for long periods in contact with strongly corrosive solutions.

A number of paints based on rubber, chlorinated or sulphonated rubber, and synthetic polymers of various types can be applied in solution or suspension. When the solvent evaporates, a film is left with some of the protective qualities of the parent substance. These paints can also carry metallic pigments and protective agents; in fact it is possible to disperse a much larger proportion of zinc in these than in drying-oil-based mixtures. Chlorinated rubber paints are claimed to resist most dilute acid solutions,[20] but the author has seen steel plates of $\frac{1}{16}$ in. thickness corroded completely through *behind* required before the surface is really sound and typical paint pinholes eliminated. An electrical company, in protecting motor casings, specify two coats of a formaldehyde-alkyd resin, followed by two of phenol-formaldehyde and one of a tinted finishing lacquer. While the covering persists, it will show the inertness of organic polymers (cf. Chapter XIX), but the risk of mechanical damage to a coating about $\frac{1}{100}$ in. thick is obvious, and rapid stripping, as with paint films, will follow local corrosion.

GLASS-LINED PLANT

Any piece of plant which is robust enough to stand heating up to 900° C. can be covered by molten inorganic enamel. The enamel coat, consisting essentially of a borosilicate glass with various additives, sets on cooling to a complete sheath for the metal below. Cast iron and mild steel are the only metals for which enamelling has been fully developed. The process can be carried out either by "dry" or "wet" methods. The first involves dusting the powdered enamel on to the hot metal, and the second spraying a wet "slip", drying, and firing. Dry enamelling gives the best and most corrosion-resistant coat, but calls for certain size limitations—not more than 500-gall. tanks.[13] In the wet process, tanks of 10,000 gall. may be treated, but are not used in very corrosive conditions. In both a smooth iron surface is prepared by sand-blasting, and two or more coats of enamel are necessary. The first "ground" coat is designed for good adhesion, and is a mixture of quartz, felspar, and borax. The final coat, for corrosion resistance, contains titania, quartz, and borax, but the actual compositions are often trade secrets.

When the coating is complete and cool, it is carefully examined for irregularities and tested with a high-frequency 10,000-volt spark discharge. Despite the partial fusion which is involved, an enamel coat usually contains a large number of small gas bubbles. The microphotographs of Figs. XII-5 and 6, shows how both methods of enamelling give this structure, with an occasional large bubble which can extend right across the whole layer. These are caused by traces of contaminating dust, and show the need for careful testing of the coating before it is put into service.

The strength of an enamelled vessel is determined by the metal, but the surface has a hardness between 5 and 6 on Moh's scale (about 400 Brinell). Thermal conductivities will vary with the enamel thickness, but a typical steel wall carrying from 0·025 to 0·05 in. will have a wall coefficient of the order of 80–100 B.Th.U./(sq. ft.)(hr.)(° F.). Hands and Whitt[14] have given a wide range of practical figures for overall coefficients when using enamel pans. The bubble structure, of course, will make for low thermal conductivity, but has been recommended as resistant to thermal shock. Enamels are chosen to match the underlying metal as closely as possible in thermal expansion, but the agreement is never perfect. A solid enamel block, with no bubbles, would be difficult to obtain and more susceptible to flaking than the normal fine foam structure.

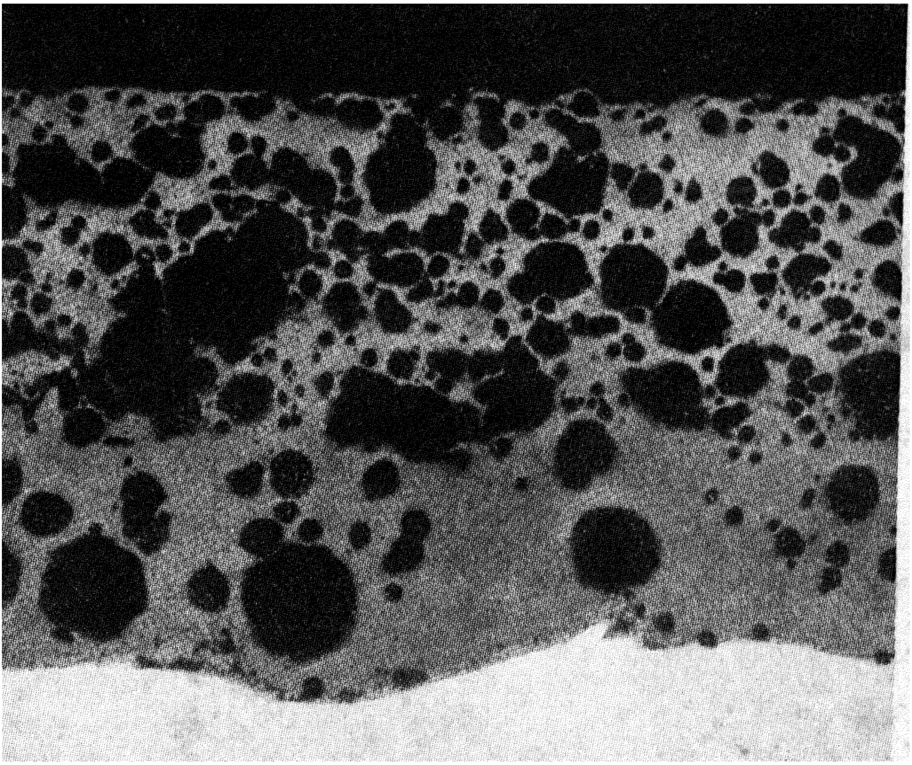

Fig. XII–5.—Wet Spray Enamel on Mild Steel.
(*Courtesy of Charlish & Healey, Trans. Inst. Chem. Eng.*, 1950, **28**, 97)

Plant for enamel covering should be designed with some care, as any change in thickness will alter rates of cooling, and sharp bends or corners cannot be properly covered.[17] When in operation the plant, of which Fig. XII–7 is typical, should be handled with respect, sudden heating or cooling being carefully avoided. An enamelled pan should not be cooled down from 100° to room temperature in less than about five minutes, and direct steam should not be turned on in the heating jacket of an empty vessel. On the other hand, provided that proper heating rates are observed, enamel is quite safe to use up to 300° with liquids and nearly 500° with hot gas.[19] When the enamel is penetrated, either by chemical action or, more frequently, by temperature stress or accident, attack by corrosive liquids can spread rapidly, and it is not possible to patch in any way. The use of tantalum or gold studs, with Teflon gaskets (Chapter XIX), has been suggested, but can only be effective with pinhole failures in their earliest stages. Adhesion is better than with any paint coating, and slightly corrosive conditions do not strip large areas after a local failure.

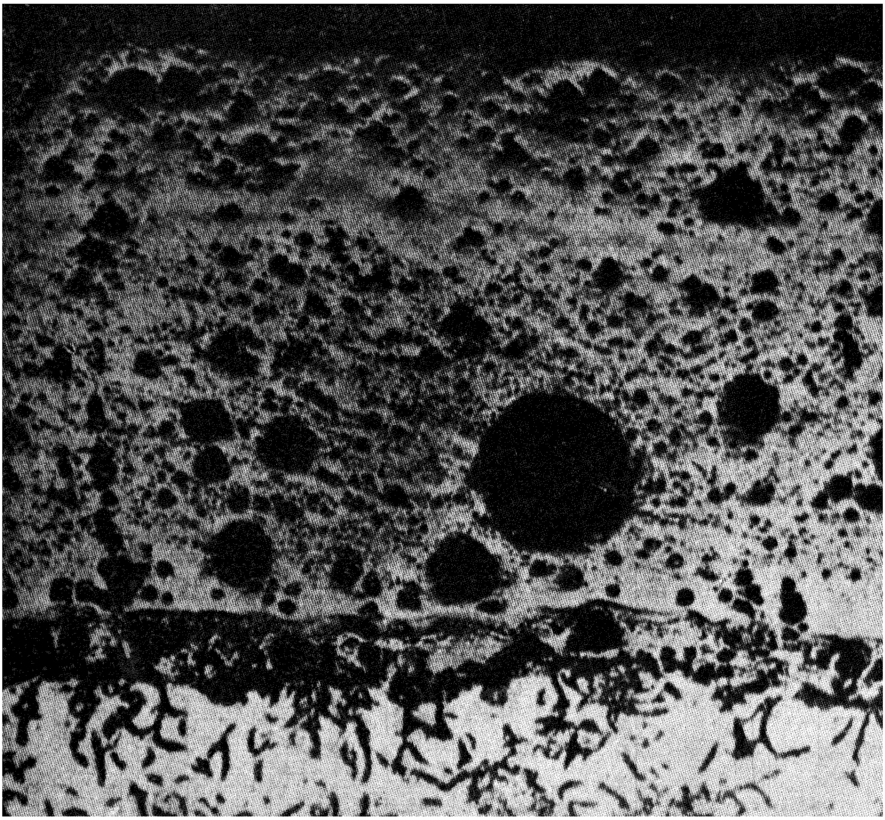

FIG. XII-6.—HOT DUST ENAMEL ON CAST IRON (×75).
(*Charlish & Healey, loc. cit.*)

The plant should not be used for any process in which alkaline solutions are often to be handled. Attack, even in fairly concentrated solutions, is not rapid, but does promote surface cracking. Such cracks soon spread on heating and the top surface of the enamel flakes away, even if the alkaline conditions are no longer present. On the other hand, all acids, with the obvious exception of hydrofluoric, and to a lesser extent hot phosphoric, have only negligible action. The rate of corrosion of boiling 20% HCl solution is only 20 mdd, which may be compared to 10 mdd for laboratory glassware. As the enamel will be about 0·4 in. in thickness, this penetration rate (of 0·012 in. per year) is more serious than would appear at first sight, but the attack is fairly even, and a life of two to three years in such circumstances does not appear unreasonable.

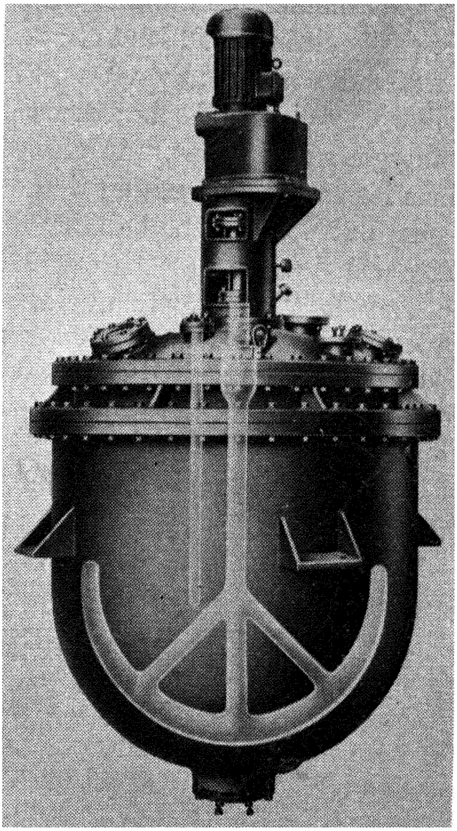

FIG. XII–7.—JACKETED ENAMELLED IRON REACTION VESSEL.
500 gals. Capacity.
(Courtesy of Cannon (Holdings), Ltd.)

No distinction need be drawn between oxidising and reducing conditions, concentrated nitric and concentrated sulphuric acids being equally inert, while bromine and iodine are quite innocuous. Enamelled iron pipes are sometimes specified for hot oleum, and the steel heat-exchangers immediately following ammonia oxidation in a nitric acid plant are coated on the nitric oxide side. Stainless steel could be used in this last case, but the enamelled construction is cheaper. When acid coolers are built in enamel, with an exposed iron surface on the water side, failure has occurred through the formation of blisters in the covering. This has been traced to leakage of acid to the water side, followed by hydrogen formation. As pointed out in Chapter I, the hydrogen can force its way into the metal and diffuse to the protected side. The enamel is not pervious to gas, and pockets under considerable pressure accumulate below, finally forcing the covering away.

Organic acids have no action, nor are they discoloured in any way, as metallic contamination is impossible. Enamelled surfaces are easily cleaned and kept clean, so that biological processes are not interfered with in any way. Plant preparations in these vessels follow very closely the lines devised on a small scale in the laboratory, using glass equipment. In view of the number of possible applications it is a little surprising that more use is not made of enamelled plant, but perhaps thc liability to mechanical damage is too great. Sizes will always be a little restricted, and heat-transfer rates cannot be very fast, if only to avoid flaking of the enamel. The cost, which varies greatly, will always be considerably more than that of the corresponding cast-iron or steel section.

REFERENCES

1. Roetheli, B. E., *et al.*, *Metals and Alloys*, 1932, **3**, 73.
2. Roetheli, B. E., and Cox, B. H., *Ind. Eng. Chem.*, 1931, **23**, 1084.
3. Gilbert, P. T., *Chem. and Ind.*, 1952, p. 354.
4. Evans, U. R., and Davies, D. E., *J.C.S.*, 1951, Part 3, 2607.
5. Parsons, A. T., *Chem. and Ind.*, 1952, p. 384.
6. Britton, S. C., "Corrosion of Tin, etc.", Tin Research Institute, 1952.
7. Rivett, F. A., *Proc. Chem. Eng. Grp.*, 1947, **29**, 3.
8. Evans, U. R., and Hoar, T. P., *J.C.S.*, 1932, **128**, 2476.
9. Hoar, T. P., *J.S.C.I.*, 1950, **69**, 536.
10. Crennell, J. T., *J.S.C.I.*, 1950, **69**, 371.
11. Mayne, J. E. O., *J.S.C.I.*, 1946, **65**, 196.
12. *Brit. Iron and Steel Res. Assn. Rept.*, J/P1, 1949.
13. MacMurray, H. D., and Currie, J. D., "Materials of Construction", p. 277.
14. Hands, C. H., and Whitt, F. R., *Trans. Inst. Chem. Eng.*, 1950, **28**, 140.
15. See, e.g., *Chem. Eng.*, 1952, **59** (Dec.), p. 155.
16. Hudson, J. C., and Stanners, J. F., *J. Appl. Chem.*, 1953, **3**, 86.
17. Jones, P. P., *Chem. Eng.*, 1953, **60** (Jan.), p. 201.
18. "Phosphating in Principle and Practice", I.C.I. Ltd., 1953.
19. Pechman, A., *Chem. Eng.*, 1953, **60** (Nov.), p. 186.
20. Seymour, R. B., and Steiner, R. H., *Chem, Eng. Progr.* 1953, **49**, 452.

CHAPTER XIII

INORGANIC CEMENTS

It is proposed to describe in this and the subsequent chapter those fluid bonding materials which act as a joint between rigid solid masses, hardening to a greater or lesser degree to form a complete solid structure. This hardening process has at least two stages as a general rule. Taking a slaked lime–sand–water mixture as an example, the first setting action is a thixotropic effect common to all solid liquid suspensions. The feeble structure of saturated $Ca(OH)_2$ solution with solid lime and sand fragments then starts to dry out, partly by water absorption in the surrounding bricks and partly by crystallisation of hydrates. As the minute hydroxide crystals begin to bind together the larger fragments the structure hardens until the cement is dry enough to take a considerable stress, as shown in the steady building up of a brick wall. Drying continues over a year or more, producing an interlacing mass of $Ca(OH)_2$, and is accompanied by a third and final setting in which the sand slowly reacts to form silicates or carbon dioxide is absorbed from the air to form carbonates. This last stage may continue over hundreds of years.

The three sets—thixotropic, drying, and chemical—are present in the action of most inorganic cements. An ideal mixture should pass rapidly through the first, and reasonably fast through the second. There should be no interruption in erection to allow joints to dry out, but on the other hand the cement mixtures should be stable enough to allow preparation in batches sufficient for several hours of work. Setting should not give any great change in volume, either by expansion or contraction, as this is bound to cause irregular movement in the masonry. In chemical plant work the final setting may be more important than in ordinary structural building, and determine primarily the chemical resistance.

LIME MORTARS

The "mortar" used for ordinary brickwork is a lime–sand mixture made from slaked lime, fine sand, and water. The usual proportions are 3 of sand to 1 of lime, with a water content ranging from 0·8 to 1·4 parts according to the taste of the bricklayer. It is seldom used for any exacting work, having little strength away from the brickwork and no real resistance to corrosion. Obviously a bond of lime or carbonate will be attacked by any weak acid, and the dried-out mixture is so porous that solutions seep in rapidly, to crystallise in the crevices with disastrous results. Lime mortar is made from "fat" limestones, nearly pure $CaCO_3$, which have the advantage that quicklime from the kilns disintegrates very completely on hydration. "Lean" limestones contain appreciable amounts of clay and sand, while dolomitic limes have a considerable proportion of magnesium carbonate. These latter, if "burned" to normal kiln temperatures of about 950°, contain "dead-burned" MgO and are slow to hydrate. A limestone which is rich enough in $MgCO_3$ can be burned to 600°–700° and then ground. The "magnesian lime" thus produced can be substituted for ordinary slaked lime in mortar. The bond becomes a network of $Mg(OH)_2$ crystals and is even more easily attacked by acids than a normal mortar. Use for ordinary brickwork is a matter of local convenience, but the lime is still unsuitable for chemical work.

HYDRAULIC LIMES

The "lean" limestones mentioned above are burned at a temperature around 1000°, when the clay and sand start to react with the lime. The complex silicates so formed do not easily combine with water, and the slaking effect which disintegrates "fat" limes dies away as the amount of impurity increases. The burned lime has then to be ground, as with magnesian limes, to obtain a reactive form for cement mixtures. On the other hand, mixtures with water will set hard even if the cement paste is used on water-submerged brickwork. Hence the name of "hydraulic" limes. The fresh-burned material contains calcium silicates and aluminates, which pass into solution and then hydrolyse, depositing a mixture of gelatinous silica and lime crystals. Such a bond is more resistant to corrosion than the mortars, but will show no advantage over Portland cement and similar mixtures.

A number of other forms of hydraulic cement have been made by mixing ground rock of suitable composition with lime. When these were developed in Italy two thousand years ago volcanic rocks "Pozzolanas"—were used, and the name is now applied indiscriminately to any cement made by mixing lime and ground siliceous material. The original "pozzolanas" were aluminium silicates with an appreciable excess of free silica, and can be duplicated by light burning (at 750°) of any siliceous clay. A joint of pozzolanic cement, as with the hydraulic limes, will be an improvement on ordinary lime mortar, but the composition is uncertain and use cannot generally be recommended.

PORTLAND CEMENT

This is the most important of all industrial cements, forming the basis of a major industry with special literature and vocabularies of its own. Portland cement is made by heating to a sintering (semi-molten) condition a mixture of crude limestone and aluminium silicates. In ordinary words, chalk and clay are roasted together, and the cement industry flourishes wherever the two can be found adjacent to good fuel supplies. The raw materials are ground into a slurry with water, and the composition carefully adjusted to give a right proportion between basic and acidic elements.

A good cement will contain: basic calcium silicate, $(CaO)_3SiO_2$; aluminate, $(CaO)_2Al_2O_3$; and ferrite, $(CaO)_2Fe_2O_3$. In the nomenclature of the cement industry these are usually written as C_3S, C_2A, and C_2F, the C, S, A, and F representing CaO, SiO_2, Al_2O_3, and Fe_2O_3. If these are taken as percentages by weight present in the final mixture, then a general formula for combination can be written as

$$C = 2{\cdot}8\,S + 1{\cdot}1\,A + 0{\cdot}7\,F$$

Generally some magnesium oxide is present, behaving as does the lime, so that a more general formula would read

$$C + 1{\cdot}4\,(MgO) = 2{\cdot}8\,S + 1{\cdot}1\,A + 0{\cdot}7\,F$$

On this basis an ideal cement mix might contain (by weight)

$$61\%\ CaO,\ 13{\cdot}3\%\ SiO_2,\ 13\%\ Al_2O_3,\ 12{\cdot}7\%\ Fe_2O_3$$

The usual mix is richer in silica and lower in alumina or iron oxide. Requirements are usually expressed in the form of ratios or "moduli". The calcium modulus, $C/(S + A + F)$, for the ideal mixture above will read

$$C/(2{\cdot}8\,S + 1{\cdot}1\,A + 0{\cdot}7\,F) = 1{\cdot}0$$

If sulphate is present, as is always the case in practice, this will remove some of the lime as a calcium sulphate, so that a typical specification[1] reads

$$(C - 0{\cdot}7\ SO_3)/(2{\cdot}8\ S + 1{\cdot}2\ A + 0{\cdot}65\ F) = >0{\cdot}66, <1{\cdot}02$$

A fairly wide range for this essential modulus can be traced in other national specifications, with a tendency towards higher values than the British.[2] The iron modulus, A/F, is set in Great Britain at more than 0·66, but the U.S.A. requires a value of between 0·7 and 2·0. The silica modulus, S/A + F, does not appear to be important, but is normally from 1 to 2, while maxima are often specified for MgO (less than 4%) and SO_3 (less than 2·75%).

The properly proportioned slurry is pumped to the cement kiln, where it is dried and heated to a final sintering temperature of about 1400°. A pebble-like cement clinker is cooled and discharged for grinding. Certain proportions of sulphate are incorporated into the mixture at this point, usually as gypsum, and the whole is ground to a powder of below 0·1 mm. Fineness is generally expressed as specific surface in square centimetres per gram, and varies from 2250 to 3250 according to grade.

The solid compounds found in cement are C_3S, C_3A, C_2S, C_4AF, free lime, magnesium compounds, and some non-crystalline glass of indeterminate composition. Of these, the C_3S is the most important, with setting properties which largely determine the behaviour of [illegible] mixture. A pure C_3S, mixed with 3 parts of sand and 0·5 parts of water, will give a primary hardening over 24 hours to a crushing strength of 5000 lb./sq. in. Over the next 300 days this increases steadily to 10,000 lb. Pure C_3A in similar circumstances sets rapidly over a few hours, generating heat and giving a friable block of negligible crushing strength. C_2S is slow to set and only develops a strength of 2000 lb. at the end of 40-day periods; the process continues, however, and the final strength is as high as a C_3S complex. C_4AF sets rapidly, without much heat evolution, and the final strength is below 1000 lb., while the other solid components do not contribute to setting properties.

It would appear, therefore, that the ideal cement would be a pure calcium silicate, C_3S, with a ratio C/2·8 S of 0·82. Alumina, however, brings down the melting-point of the cement mixture and tends to form a solid C_3S phase in the kiln. As a result, it is necessary to keep the alumina content above 6%, despite the formation of undesirable C_3A. Iron oxide behaves in the same way, improving the of cement—but the concrete suffers as a result. The high-alumina cements described below can sometimes be used in these conditions. If concrete is laid in very large masses, the heat slowly evolved on setting may cause deterioration, and a special low-heat cement should be used.[3, 18]

It is probably better to "proof" all concrete in some way, and certainly some form of surface treatment should always be given when the cement surface is to resist the action of chemicals. The simplest and easiest way is to brush over with a 10% solution of sodium silicate. This will precipitate gelatinous silica in all the surface pores, and reduce seepage to a very small figure. Even better deposits can be obtained with proprietary compounds containing magnesium fluosilicate or silicon esters, while an alternative for *water* proofing is rubber, brushed on to the dry concrete in the form of a solution in thinning naphtha. The cheapest form of treatment is by tar or bitumen emulsion, as in road work. Synthetic resins of neutral or basic type may be substituted for the rubber to give resistance to solvents, and the new silicone resins have been claimed[4] to give excellent results, but may be expensive. A concrete surface can be rendered sterile by covering with neat cement containing up to 10% of copper acetoarsenite. This will poison micro-organisms very effectively, and though originally used as a means for killing "athlete's foot" fungi, will keep down algae in cooling ponds.[5]

Corrosion Resistance

The resistance of concrete to chemicals is essentially that of a series of inert siliceous particles joined together with a bond of reactive silica and calcium hydroxide. Any strong alkali will slowly leach out the silica, while an acid will react at once with the free lime. Only neutral or weakly alkaline solutions are inert, but may penetrate the pores and there crystallise, disintegrating the structure. Sulphate solutions are particularly active, due to the formation of complex sulpho-aluminates, but other salts are not quite so destructive, and it is possible to use large concrete tanks for storage of sea water. Unless the plant is very large, it is better to use either high-alumina or blast-furnace cement (see below) for all containing vessels, and reserve the cheaper Portland cement for building, brickwork joints, and floors. If used, it should always be proofed, as indicated above. Petroleum and tar oils can safely be stored in tanks made from Portland cement, however, though the joints between layers must be carefully made and a softened surface skin left undisturbed. Reinforced-concrete containers are sometimes built to stand internal pressures up to 75 lb./sq. in., allowing a safe stress of 150 lb./sq. in. in the shell.[6]

Floors in most industrial buildings are made up from concrete, with or without reinforcing, and are expected to stand up to spillage and hard wear. Fatty oils of any type tend to hydrolyse in contact with the lime of the cement, and the acid salts so formed disintegrate the surface rapidly. Milk spilled on a concrete floor and left to dry is particularly destructive, and so are all sugar solutions. Careful washing and preproofing can improve matters, but where active corrosion of any type is expected some other form of flooring must be used. Good quality brickwork is commonly laid with cement mortar, and this should always be done for buildings housing chemical plant. The attack of acid fumes is confined to the surface of the bond, and provided that the softened surface layers are undisturbed, the bulk of the cement remains stable. Buried foundations laid in cement are subject to attack by sulphate-bearing water; where local samples show more than about 0·1%, these foundations must be sheathed in some way. Cases of attack by sulphur bacteria have been recorded.[17] It is recommended, finally, that all cement joints in any form of chemical plant be made from either blast-furnace or high-alumina cement.

PORTLAND BLAST-FURNACE CEMENT

The slag from iron blast-furnaces, usually obtained in a coarsely granulated form, has a composition which in general contains less calcium and more (silica + alumina) than a properly proportioned Portland cement mix. As it is obtained incidentally in the manufacture of iron, the composition can vary widely. A series of samples listed by Parker and Nourse[7] showed CaO contents from 31% to 53%, SiO_2 from 29% to 40%, and Al_2O_3 from 7% to 22%. These slags are mixed with one to two parts of Portland cement clinker, the usual gypsum adjustment added, and the whole ground to normal cement fineness. Specifications[8] call for not more than 65% of slag, and the resulting cement–sand–gravel mixture has the same strength at 100 days as a Portland cement concrete, though somewhat slower in set (Fig. XII–3). The mixture is actually cheaper than Portland cement in most industrial localities, and has the added advantage of increased chemical resistance.

Owing to the wide variation in composition, standard "moduli" for blast-furnace slag cement have not been rigidly laid down, but the ratio $(CaO + MgO + \frac{1}{3}Al_2O_3)/(SiO_2 + \frac{2}{3}Al_2O_3)$ is usually from 1·0 to 1·2. The amount of water added is more important, and should be rigidly controlled at 0·45–0·5 parts to 1 part of cement, for any normal blast-furnace cement concrete. A mixture with sand and gravel should contain rather more cement than the ordinary Portland mixes, and the ratio 1:2:4 is seldom departed from in good practice.

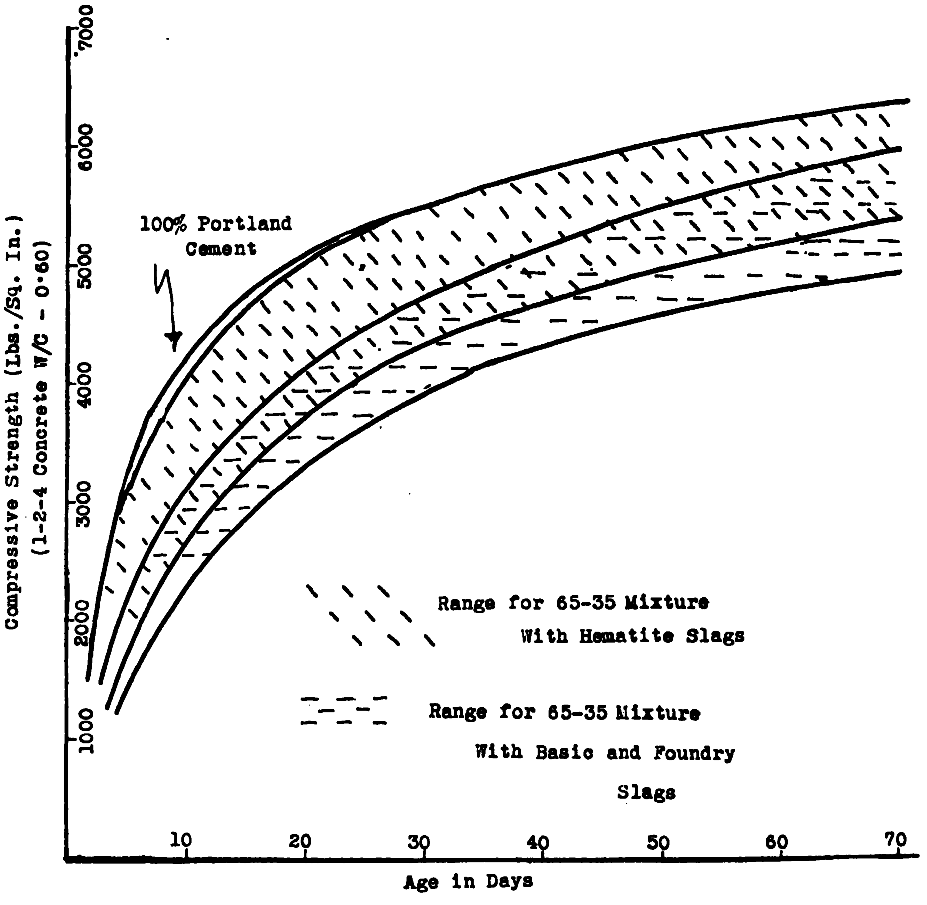

Fig. XIII-3.—Setting of Portland Cement, Portland—Blast-furnace Cement.

(After Parker & Nourse, *Granulated Blast-furnace Slags*, H.M.S.O., 1949)

Other blast-furnace cements are sometimes used, with more slag than the standard type. Some slags, finely ground, can be used direct without incorporation of any Portland clinker. A "super-sulphated" cement contains up to 85% of slag and a very high SO_3 content in the finished product (5–9% SO_3). Use is a matter of local convenience, as these mixtures appear to be very similar to the ordinary Portland blast-furnace cement in behaviour.

Corrosion Resistance

The main advantage of these materials is greatly increased resistance to sulphate attack. The bond is still porous, and concentrated salt solutions can disintegrate by crystallising, but the very dangerous sulpho-aluminates are no longer formed so readily. The "super-sulphated" variety is particularly recommended for sulphate solution storage. All dilute neutral solutions can be stored in Portland blast-furnace concrete tanks, though nitrates have been said to give some disintegration. Dilute acids are relatively inert, and the cement can be used for drains down which acidic wastes from breweries and dairies are discharged. Acid resistance would be expected from the lower content of calcium, but the silica bond is not readily attacked by alkalies, and dilute caustic soda (about 1%), which would disintegrate other cements, is inert. This is a useful advantage over the acid-resistant high-alumina forms described below. Surface proofing with silica-depositing solutions is inadequate, and rubber or synthetic resin solutions must be used.

HIGH-ALUMINA CEMENT

Bauxite and limestone are sintered to form a crude calcium aluminate, and the mixture ground to the same fineness as ordinary Portland cement. The composition corresponds approximately to $(CaO)_5(Al_2O_3)_3$, with up to 5% of silica as an impurity. Specifications[9] call for an alumina content of not less than 32%, while the A/C ratio should range from 0·85 to 1·3. The mixture is marketed under various trade names, of which "Ciment Fondu" is the best known in Europe. As might be guessed from the need to restrict the set of "C_3A" in Portland cement, these mixtures harden rapidly. The heat developed becomes a problem when the cement layers are more than two or three inches in thickness, but is an asset when building under freezing conditions. If a wall built in Ciment Fondu is protected from freezing over the first four hours, the heat developed will ensure complete setting with atmospheric temperatures well below freezing-point. Although the total heat given out is no greater than for ordinary Portland cement, it is all liberated over a much shorter period, at maximum rates up to 9 gm. cal./(gm.)(hr.). As a result of such changes, concrete from high-alumina cement can have a compressive strength of 7000 lb./sq. in. in 24 hours, and reaches load-bearing conditions far faster than an ordinary Portland cement concrete. The relative setting rates of these two materials are set out in Fig. XIII-4.

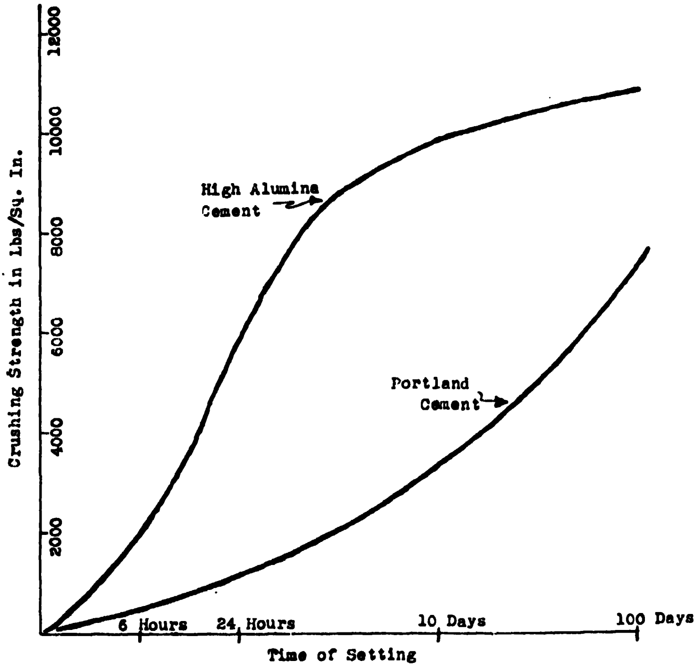

Fig. XIII-4.—Setting of Alumina and Portland Cements.

Set is due, in the first place, to hydration of calcium aluminates to form complex solid hydrates. These harden further, especially above 25° C., to form a very stable complex, $Ca_3Al_2(OH)_{12}$. This crystalline arrangement does not break down appreciably on heating or even dehydrating, and as a result the cement bond retains strength and form to unusually high temperatures. (This property will be referred to in the chapter on Refractories.) Mixtures of alumina cement with sand, gravel, and water are made up in just the same way as for Portland concrete, though the very inert nature of the bond makes all sorts of fillers possible. Crushed calcium sulphate, for instance, has been recommended, while all sorts of "foamed" rocks and slags are built up into insulating concrete plasters. The porosity of the cement bond is less than either Portland or blast-furnace, but on the other hand it cannot be proofed at all by silica deposition. A drying oil (linseed or tung), as used in paints, has been suggested, while any rubber or resin solution should give satisfaction. A polyester resin gives a dust-free finish in cosmotron work.[16]

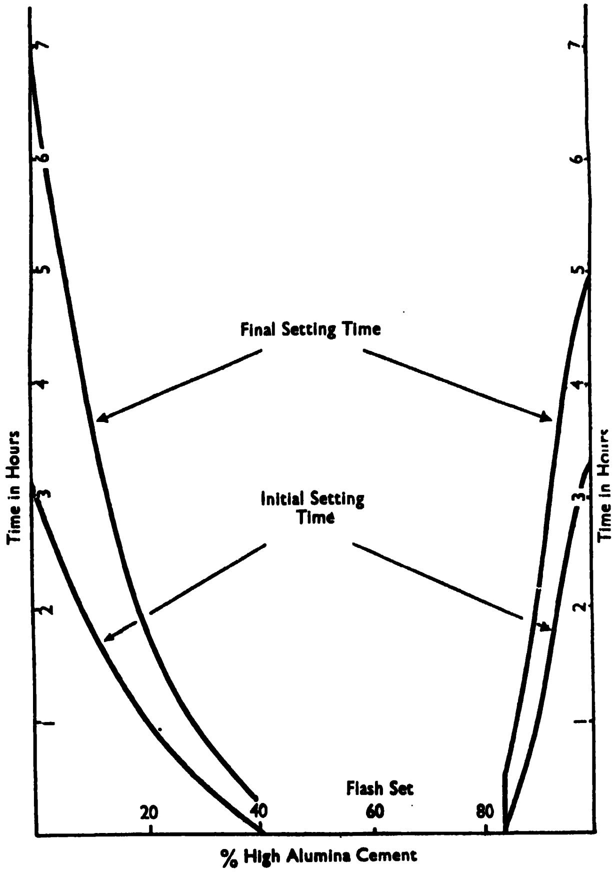

FIG. XIII-5.—SETTING TIMES FOR MIXTURES OF ALUMINA AND PORTLAND CEMENT.

In working with high-alumina cement it is necessary to avoid mixing with small quantities of ordinary Portland cement. The effect of such blending on setting time is shown in Fig. XIII-5. Mixtures in the flash-set zone give a very weak bond, even if the slurry can be put in place before setting. It is possible, using due care in compounding, to work with mixtures when very rapid repairs are required, but this can only be in an emergency.[10] If either Portland or alumina cement is hardened properly, the other can be bonded to it with a perfect bond as strong as either of the pure mixtures.

Corrosion Resistance

Reaction with cold dilute acid solutions (below 0·5%) is very slight, especially with sulphuric acid. Quenching of ashes gives a dilute sulphuric-sulphurous acid which disintegrates ordinary concrete but has no action on alumina cement mixes. The vast bulk of feebly acidic industrial effluents are without action, and where acid splashing can occur it is desirable to set masonry in alumina cement mortar. Sulphate solutions can only attack through crystallisation effects, and the lower permeability allows the storage of stronger solutions. Bleaching vessels for paper manufacture, using sulphur dioxide as a bleaching agent, can be constructed entirely in alumina cement concrete. Sodium sulphide solutions, used in leather treatment, are applied to the hides in alumina cement tanks, with avoidance of metallic contamination. A very impressive list of chemicals handled successfully in alumina cement containers is given by Hussey and Robson,[11] and it is clear that much better resistance in all neutral or acid conditions can be obtained than with any of the alternative cements. Unfortunately, the alumina bond is not stable in contact with alkalies, and in these circumstances Portland blast-furnace or supersulphated cement should be used.

It will be appreciated that the cement is not acid-resistant in the way that, for instance, mixtures of asbestos and sodium silicate are resistant. Nevertheless, where dilute acid solutions are handled in large quantities, or acid-bearing gases may cause condensation, the possible use of alumina cement mixtures should be studied.

BARIUM AND STRONTIUM CEMENTS

It is possible to make up cement mixtures in which the calcium is replaced by strontium or barium, the quality being improved rather than otherwise. Barium compounds have the property of resisting penetration by radioactive phenomena, and may become much more important in future years. The shields for atomic piles are normally made up in barium cement. A typical mixture will contain tribarium silicate, $(BaO)_3 . SiO_2$, having setting qualities not unlike those of the calcium compound, and alumina-iron complexes of various forms. A pure tribarium silicate would contain just under 90% by weight of barium oxide, but cements so far manufactured have only been about 50% BaO.[12] The final bond of such cements is not only resistant to X-rays and similar radiation, but much more resistant to salt solutions, including sulphates. Water washings from these cements are not toxic, as the barium is converted into insoluble compounds. Strontium cements are similar to the barium compounds, except that they are not so resistant to radiation.

MAGNESIAN CEMENTS

These are known as "Sorel" cements, after their inventor, and are made up from mixtures of magnesium chloride and calcined magnesia. The ground oxide, containing not less than 87% of MgO,[13] is mixed with a concentrated solution of magnesium chloride (25–30% by weight $MgCl_2$). Set is rapid, a complex magnesium oxychloride being formed. The precise composition of the cement mixture has not been specified, but it is generally agreed that the three components shall be present in the molar proportion MgO(3–5), $MgCl_2$(1), H_2O(12), or about 1·5:0·8:1·8 by weight. The mixture can be used alone, or combined with an inert filler to form a very dense and hard surface, with excellent wearing qualities. Iron is attacked by the chloride, so reinforcing is undesirable, while water slowly disintegrates the bond. A Sorel cement flooring is therefore spread as a surface over ordinary concrete, and waterproofed by wax or linseed oil films. In view of this general reactivity, magnesian cement mixtures are not recommended for chemical plant.

SILICATE CEMENTS

Bonding plasters made up from sodium silicate (waterglass) were the first and are still the most important of all acid-resistant jointings. Waterglass is an aqueous sol of sodium silicate and silica containing up to 40% of solids. It can be used as an adhesive by itself, drying as it does to a firm jelly, but in acid-resisting cements the waterglass is mixed with an equal weight of filler (asbestos powder, sand, slate, or graphite) and used in such a way that a deposit of hydrated silica forms over the bond surface. In the early days of the acid industry joints between acid-resisting stoneware blocks were made with a simple asbestos-silicate paste and brushed over with acid before use. Now it is common practice to incorporate a "catalyst" which develops acidity on standing, sodium silico-fluoride or ethyl acetate being the most usual agent. As the acidity produces an irreversible set at fairly high rates, the cement must be made up in small quantities and used at once. If no acid-forming agent is present, setting is very slow, and up to 10% of ordinary Portland cement should be incorporated to allow ordinary bricklaying to proceed. This addition cuts down the corrosion-resisting qualities of the bond.

A joint between ceramic bricks or tiles is always the weak point in an acid-resisting structure, and must be made as thin as possible. The masonry shapes must be carefully cut and fitted, while the cement should be mixed exactly as directed by the makers. Traces of lime or acid left in mixing troughs will give a "flash set", and similar action at the brick surface is responsible for some of the seepage often noticed in plant work. It is claimed[14] that cements using ethyl acetate as a setting agent are less susceptible to this "wick" action than others. When properly made and kept wet, a joint of silicate cement lasts indefinitely in contact with any acid except HF and H_3PO_4. If allowed to dry, the cement shrinks and becomes porous, even if the joints do not break away from the bricks. All plants lined with silicate-jointed masonry should therefore be kept full of dilute acid when not in use.

The final bond is hard, inflexible, and brittle, but is the only joint that will stand up indefinitely to boiling sulphuric and nitric acids. The maximum working temperature is commonly set at 550° C.,[19] but bricks set in silicate cement have done excellent service in a Gaillard acid concentrator at considerably higher local temperatures. As mentioned above, the only acid attacking rapidly is hydrofluoric, while hot concentrated phosphoric has some limited action. On the other hand, all alkaline solutions attack and disintegrate the cement, while even a neutral boiling water will have more effect than boiling sulphuric acid. Plants should never be cleaned with alkaline detergent or hosed down freely with hot washing water. As the joint is not used for floors, such treatment is unlikely, but the contingency should be borne in mind. Silicate cements form much too brittle a bond for use in laying flooring tiles, and any mechanical stresses should be avoided.

A mixture based on potassium silicate has been claimed by makers to resist very dilute or very concentrated acid better than the cheaper water-glass cement.

SULPHUR CEMENTS

As the primary materials for these cements are sulphur and sand, they are classed among the inorganic cements, but it is quite common to obtain a more elastic joint by the addition of organic plasticisers. A typical mix will contain 2 parts of sulphur to 1 of fine sand, with up to 0·2 parts of a sulphur-bearing resin or bitumen. The mixture is fluid enough at 140° to pour into the joints between heated bricks or tiles, and cools to a firm resilient bond, very suitable for flooring. As there is marked shrinkage on cooling, the bond is made up with two or three pourings, but the joint with the brickwork does not break, and will stand reheating to almost the pouring temperature. A maximum working level of about 80° C. is usually recommended.[15]

This bond is resistant to all dilute acids, even to HF solution, but strong oxidising solutions react with the sulphur, while caustic alkalies and oils have some solvent action. In these circumstances the principal use lies in the construction of acid-resistant floors, for which the more stable silicate cements are too brittle. Caution is required in working with a sulphur cement, especially if it has been plasticised with a coaltar pitch, as severe cases of dermatitis have been traced to this cause.

Sulphur and silicate cements are the cheapest of acid-resisting bonding agents, costing at most (1952) some £80 per ton. Were litharge–glycerine mixtures not so expensive they might rank as competitors, but these well-known laboratory tools are much too costly for large-scale use.

REFERENCES

1. B.S. 12 (1947).
2. See, e.g., International Specifications, *Cement and Lime Manfr.*, 1949, **22**, 41 and 64.
3. B.S. 1370 (1947).
4. *Chem. Eng.*, 1951, **58** (Nov.), p. 208.
5. *Ind. Chem.*, 1952, **28**, 399.
6. Lewaren, S. W., *Concrete Const. Engnr.*, 1950, **45** (No. 2), p. 41.
7. Parker, T. W., and Nourse, R. W., "Granulated Blast-furnace Slags", H.M.S.O., 1949.
8. B.S. 146 (1942).
9. B.S. 915 (1947).
10. Robson, T. D., *Chem. and Ind.*, 1952, 2.
11. Hussey, A. V., and Robson, T. D., "Materials of Construction", p. 25.
12. Braniski, A., *Cement and Lime Manufacture*, 1950, **23**, 30.
13. B.S. 776 (1938).

14. Ward, R., "Materials of Construction", p. 17.
15. Steiner, R. H., and Pascoe, W. R., *Chem. Engng. Progr.*, 1953, **49**, 110.
16. Anon., *Ind. Chemist*, 1953, **29**, 119.
17. Taylor, C. B., and Hutchinson, G. H., *J.S.C.I.*, 1947, **66**, 54.
18. National Building Studies Bulletin No. 3. "Concreting, etc., in cold weather." H.M.S.O., 1948.
19. See, e.g., Seymour, R. B., and Steiner, R. H., *Chem. Engng. Progr.*, 1953, **49**, 158.
20. Carman, P. C., "Chemical Constitution and Properties of Engineering Materials." Edward Arnold, 1949, pp. 455 *et seq.*

CHAPTER XIV

ORGANIC CEMENTS AND LUTING MATERIALS

ASPHALT

THIS common cementing material is a mixture of inorganic filler with either natural bitumen or a distillation residue from petroleum or coal tar. It is quite solid at ordinary temperatures, but can be brought into a soft plastic condition by heating to about 200° C. "Mastic asphalt" was originally used in the form of natural rock asphalt—a bitumen-impregnated limestone—and limestone is still the most usual filler for the various grades of synthetic product. These are used in building and are not the right material for use where acid attack is expected. Sand or slate filling, ground to a specification such as "all through 7 mesh, 50% through 200 mesh", must be substituted. The great advantage of any proper asphalt layer is that it is completely waterproof, and prevents that slow seepage of aqueous solutions which so often destroys concrete. Essentially unreactive, it can be laid over any form of concrete, timber, or metal, and often forms a proofing layer between two reactive surfaces such as concrete and lead.

As a floor in chemical plants handling aqueous products, asphalt is very widely used, and specifications[1] have been drawn up for such work. These call for a careful sizing of the aggregate, and a soluble bitumen content of 11·5–18%. The specific gravity of the bitumen must exceed 1·0, while hardness and non-volatility are also called for. The wearing qualities of the finished floor can be adjusted by increasing or decreasing the organic matter content, while a certain proportion of large aggregate, up to ⅜ in. in size, can be worked into thick layers for heavy duty. Most chemical plant flooring comes under this category, as distinct from office floors built for quiet and comfort of workers, and should normally embody an asphalt layer of not less than 1 in. in thickness. It will generally be black in colour, though coloured forms are available,[2] and the filling is sand as a rule. This sand must be ground rather more finely than limestone to give the same compounding hardness—a difference bound up in the nature of the solid surfaces. Laying of such asphalt floors is very straightforward if the underlayers are dried out thoroughly beforehand—this is absolutely essential.

Corrosion Resistance

Even a limestone-based asphalt will resist the spillage of hot inorganic solutions provided that it is washed down frequently. Streams of hot water directed at one spot will cut a groove and ultimately penetrate the asphalt—a frequent cause of failure with drainage channels. Alkaline solutions are quite inert and so are dilute acids, while strong mineral acids in momentary contact with the floor are not a danger if they can be washed away rapidly. Owing to the ductility of the flooring—a necessary property—it is not possible to avoid indentations or wear depressions. These in time cause a tendency for pools of liquid to form and perhaps concentrate to a corrosion level. For this reason all floors should be laid with a definite slope towards a drain—inclinations of up to 1 in 60 have been suggested. Projections through the flooring, such as steel girders carrying plant, should be covered with asphalt to a point well above any likely splash level (Fig. XIV-1). Asphalt does not seal well to metal, and straight joints lead inevitably to seepage and corrosion.

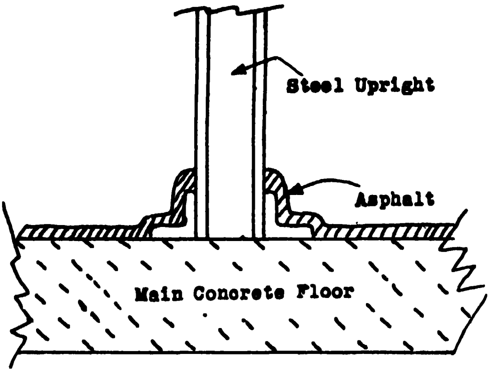

FIG. XIV-1.—ASPHALT FLOOR PROTECTION.

Organic liquids are much more of a problem. Light solvents disintegrate the asphalt at once, while mineral oils of any kind soon soften the flooring to a dangerous level, besides producing slippery spots which may cause accidents. Fats, fatty oils, organic acids, and sugar solutions all attack to some extent, and it is best to avoid asphalt in plants where these are being handled. One particular field of organic chemistry, the manufacture of high explosives, calls for a sparkproof floor, preferably with good electrical conductivity. This means that no possibility of local high temperatures should exist, and the floor should be nearly frictionless. An asphalt floor, with finely ground barytes used as a filler, has answered satisfactorily all tests for local heating and sparking, while the incorporation of coke or carbon dust confers a substantial degree of electrical conductivity.[3, 11]

When asphalt is used in the lining of tanks or containers, it must stand up to more severe conditions than simple flooring. Both the filler and the bitumen must be as unreactive as possible. The latter will generally contain both acidic and unsaturated hydrocarbon complexes, which help to build up the colloidal structure characteristic of the bitumen. Preferential attack on any component can cause gradual disintegration, while it can no longer be assumed, as with flooring, that the temperature remains at ordinary levels. The working temperature of an asphalt lining should never exceed 65° C., which may call for an inner coating of brickwork to protect the liquid-proof asphalt seal. With the recent development of inert organic polymers, a different lining would probably be chosen for high-temperature work. For temperatures up to 65°, the linings have been found suitable for a wide range of aqueous solutions, including hydrochloric and sulphuric acids of all strengths up to 25%.[4] A combination of asphalt backing with acid-resisting tiles, laid hot in the asphalt, and "pointed" with a sulphur or resin cement (Fig. XIV-2), is almost impervious to any cold inorganic acid, and has proved itself in the building up of metal pickling baths or acid-resisting ducts. Such plant is simple to construct, with no limits on size, and is relatively cheap.

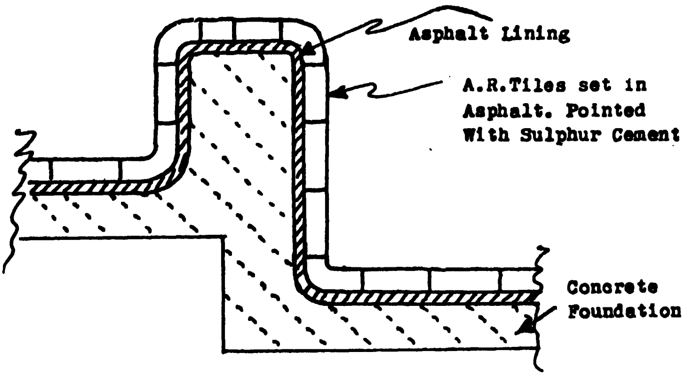

FIG. XIV-2.—SECTION THROUGH ACID PICKLING BATH WALL.

LATEX CEMENTS

These could be dealt with under several headings, as they consist of Portland (Alumina) cement, sand aggregate, and a rubber or resin latex. Mixtures will contain up to 6 parts of solid to 1 of latex, made up in the same way as for ordinary cement–aggregate–water concretes. Setting is rapid, even with Portland cement component, and complete in four hours, so the mix should be made up in small batches and used immediately. It is rather sticky in texture, and cannot be spread so easily as ordinary concrete. When used as a surfacing rather than a jointing material it is spread in thin layers over, e.g., ordinary concrete, to which the adherence is quite good. The surface obtained is resilient, impervious, and very resistant to abrasion, especially when rubber latex has been used. Joints between tiles or similar shapes are much more elastic and tough than a cement bond, and latticed iron grids filled and joined by latex cement have been recommended for heavy industrial work.

Corrosion Resistance

This is unusually good because of the dual nature of the bond. Chemical reagents may leach away the inorganic cement, but leave a skeleton of sand imbedded in rubber or resin, and resistant to nearly all inorganic solutions. An oil or grease will swell and weaken the rubber, but the cement holds the expanded mass in position. In both cases the surface layers only are attacked, and the stable reaction products protect the underlying joint. If the rubber latex is replaced by one made from neoprene or polyvinyl chloride (Chapter XIX) resistance to grease and oil increases, while alumina cement strengthens the bond in the presence of acids or sulphates. Latex mixtures may be widely used in the future as a final covering for cement floors, though they may never be so waterproof and corrosion-resistant as a good mastic asphalt in contact with aqueous solutions. The cost of latex cements is rather high at the moment, but rubber prices have fluctuated so widely of recent years that any price predictions will be very uncertain.

ACID-RESISTING RESIN CEMENTS

These have been developed as an alternative to the sodium-silicate-based mixtures which have given service for so many years. It is not difficult to make a corrosion-resistant resin, but not so easy to confer on it the properties of a good cement. Most success has been achieved with a partly polymerised liquid resin of the phenol-formaldehyde type, which is mixed shortly before use with a solid aggregate containing a catalyst for final setting of the resin. Polymerisation is just as subject to temperature restrictions as is cement setting, and joints should never be made with atmospheric temperatures below 10°. On the other hand, if air temperatures exceed 25°, the liquid syrup is prone to run out of the joint before set is complete. All joints should be thin, as with silicate cements, and temperatures can usually be adjusted by heating or cooling the bricks. Setting is complete after about 48 hours and adherence to all types of brickwork is good. In order to compete in price with the inorganic cement, it is necessary to use crude phenol mixtures rather than a pure product. A mixture made from cashew-nut oils compares favourably with one from mixed tar acids, while of late a furane resin, made up from furfuryl alcohol, has been developed in the U.S.A. Development in this field has quickened and other mixtures may soon have a working history.[8]

Corrosion Resistance

All these resin bonds withstand dilute acids well, even at boiling-point, though a furane resin is not recommended for nitric acid or other oxidising agents. Hot sulphuric and nitric acid of above 30% in strength will attack all three forms, and for these conditions only a silicate cement is really suitable. Alkaline solutions attack a phenol-formaldehyde complex slowly, have less action on cashew-nut resin, and still less on furane forms. The limiting temperature for the first two is about 140°, but the last has been used, combined with glass cloth, to give an impervious backing at nearly 200° C. It forms a very useful alternative to asphalt for the outer lining of an acid pickling bath working at high temperatures. Furane and cashew-nut resins appear to give a still tougher bond between tiles than sulphur cements, and were they cheaper (cost in 1951–2 about £300 per ton) they could be widely used in all bonding purposes for corrosion-resistant walls or tiling.[9, 10]

LUTING AND PACKING MATERIALS

Many of the brittle acid-resisting materials used in chemical plant require a soft joint packing which can fill in the spaces between a spigot and a faucet—the typical joint for such plant, as shown in Fig. XIV–3. This shows a stoneware pipe connection, in which the preliminary jointing is a ring of asbestos rope, followed by a packing of putty made from china clay, asbestos fibre, and mineral-oil jelly. Such a combination stays soft indefinitely and can be used in contact with all normal acid fume.[7] The relative proportions are not important, and vary from one works to another, but a reasonable stiffness is given by approximately equal parts of the three components.

If the mineral-oil jelly is replaced by linseed oil, a putty is obtained which is less subject to softening when warmed. Generally rather less oil is used, but a mixture with 60% asbestos, 10% china clay, and 30% boiled linseed oil will stand up to most cold mineral acid mixtures. The joint can be faced on the outside with a thin layer of rapid-setting silicate cement. Coal tar and tar oils have been recommended[5] as a basis for putties to resist hydrochloric acid, and a very simple cheap mixture can be made from china clay, asbestos wool, and dehydrated tar.

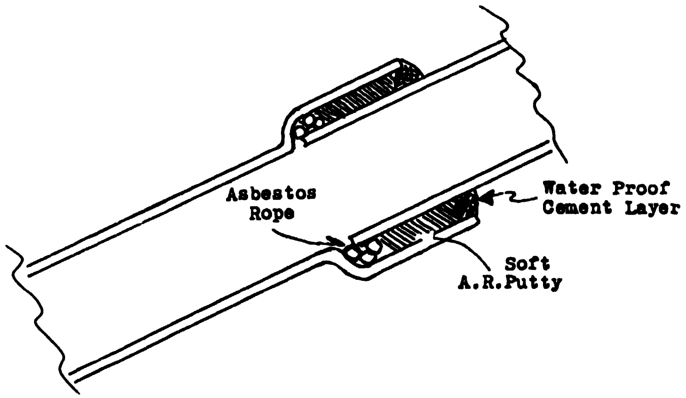

FIG. XIV-3.—SPIGOT-FAUCET JOINT IN A.R. STONEWARE PIPE.

Asbestos is so freely used in compounding soft jointing mixtures that, although inorganic, its properties may be briefly listed here. As a hydrated magnesium silicate, containing up to 15% of lime and various other ingredients, it is fire-resistant, but starts to lose water at about 600° C. The dehydrated threads have no longer any appreciable strength and all jointing properties are destroyed. A "blue" asbestos, containing iron, is the most acid-resistant form, but all pure mineral asbestos is good, especially when clamped between metal flanges which hold corrosion products in place. The most common asbestos joint of commerce, also known as a "fibre" joint, is made up from asbestos fibre and rubber solution, hot-rolled to the fibre sheets from which shapes are cut. The best grades will stand steam at pressures up to 1000 lb./sq. in., but are clearly not resistant to solvents or to strong acids. Joints for these should be cut from blue asbestos cloth or millboard, without the cotton admixture which is common in cheaper grades of commercial asbestos. While soft and easily made, these closures are not tight to very high pressures, and metal-reinforced threads or shapes have been used. The introduction of polythene and teflon has provided a valuable alternative in such cases (Chapter XIX). The packing for pump glands is normally a heavily greased woven thread, with graphite incorporated in the weaving; for acid pumps the thread can be of asbestos, and perhaps the additional strength of cotton incorporation is not out of place in this sphere. Asbestos cannot be built up by artificial synthesis, at any rate in satisfactory form, and industry relies on the natural product.[6]

Cork joints were widely used in Germany during the period 1939–45 as a substitute for asbestos or rubber, and can be made to withstand water or solvents at temperatures up to 150°. The wood fibre will hardly resist strong acids, but may have some advantage over rubber for solvent plant.

REFERENCES

1. B.S. 1076; B.S. 1410.
2. B.S. 1451.
3. B.P. 500,650.
4. Broome, D. C., "Materials of Construction", p. 75.
5. Greenwood, H. D., and Snelling, F. C., *Proc. Chem. Eng. Grp.*, 1937, **19**, 90.
6. Cf. B.I.O.S. Rept. 404, F.I.A.T. Rept. 1070.
7. Ward, R., *Industrial Chemist*, 1944, **20**, 283.
8. Seymour, R. B., and Steiner, R. H., *Chem. Engng. Progr.*, 1952, **48**, 650; 1953, **49**, 220, 276.
9. Evans, V., *Proc. Chem. Eng. Grp.*, 1953.
10. Earp, F. K., Shapiro, F., and Wiggs, A. E., *ibid.*, 1953.
11. See also "Floor Finishes for Industrial Buildings", National Building Study No. 11, H.M.S.O., 1952.

CHAPTER XV

BRICKS, TILES, AND STONEWARE

A BUILDING to house chemical plant may be constructed in reinforced concrete, but is quite generally built from ordinary bricks and mortar. This latter is still the simplest way in which to build a convenient shell for plant and provide protection from wind and weather. There is some doubt whether bulk production of all types of chemicals should not be carried out in the open,[1] with indirect automatic control and only the operating panels housed, but even for these a brick construction is quite usual. The load-bearing capacity of good brickwork is a great asset for improvised addition to plant, and the depreciation rate is negligible. Many brick buildings erected fifty years ago in acid plants are still doing excellent service in some capacity. Special bricks and tiles for acid resistance are even more long-lived, while stoneware drains put down in early Roman times are giving excellent service today.

BUILDING BRICKS

Normal building bricks are now approximately 9 in. by 4 in. by 3 in. in size, though there are interesting local variations.* A cubic yard of brickwork contains some 380 bricks, with 6–7 cu. ft. of mortar. The brick will be laid in a wide variety of walls, with bonds of century-old tradition. Thus a course laid as in Fig. XV–1 has alternate "header" and "stretcher" bricks, and is laid in "Flemish bond", while "English bond" has alternate courses of

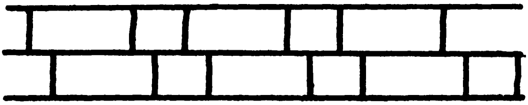

FIG. XV–1.—FLEMISH BOND BRICKWORK.

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* B.S. 657 (1950) specified $8\frac{3}{4}$ in. × $4\frac{3}{16}$ in. × $2\frac{7}{8}$ in.

"headers" and "stretchers" as in Fig. XV–2. Properly laid brickwork will take loads up to 100 lb./sq. in. with absolute safety, even if "common" brick is used. When a Portland cement mortar is used, the ultimate strength is that of the brick itself. The porosity, measured by the gain in weight on immersion for 5 hours in boiling water, is probably more important than strength for chemical plant purposes. An alternative measure is given by 24 hours' steeping in cold water; this is lower than the boiling-water figure, and the ratio of the two is sometimes known as the "saturation coefficient".[10] The normal figures for building bricks are set out in Table XV–1.

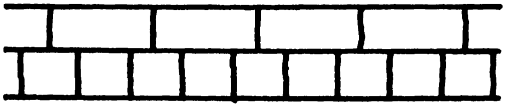


FIG. XV–2.—ENGLISH BOND BRICKWORK.

TABLE XV–1[2]

	Crushing Strength	Porosity
	lb./sq. in.	(%)
Common Brick	500–5000	10–50
Machine-made Brick	750–10,000	3–50
Hand-made Brick	1000–8000	10–50

The wide variation in strength and porosity reflects local methods of manufacture with a range of materials found on the spot, as this largely eliminates transport charges. All sorts of clay are utilised, with addition of lime and alkalies to give a lower fluxing temperature and a firing range for manufacture of 800°–1000° C. As a result, the maximum working temperature for ordinary brick is only about 400°, and this combined with high porosity rules out extensive use in chemical plant. Normal building design must provide for protection from wetting and frost effects, while any solution which can seep into the pores and deposit solid will be just as disruptive as ice formation. There is ample surface exposed to any type of chemical attack, when strong acids or alkalies can disintegrate the brick entirely. The author has seen brickwork piers below the floor of a caustic soda plant reduced to a mass of loose rubble by accidental spillage, while draught fumes containing an unduly high proportion of sulphur dioxide almost destroyed a heavy chimney wall in less than twelve months. Careless manufacture and burning often gives bricks with an appreciable amount of free lime, which gradually hydrates and disintegrates the fired clay. This is bad manufacture, but it reinforces the argument that ordinary building bricks should not generally be used in chemical plant. The same is true of "sand-lime" bricks, made from a mortar of low lime content and "cured" to permanent shape in steam-heated kilns. Studies of clay, sand-lime, and concrete building shapes have been presented in the form of Bulletins by the Building Research Association.[2, 3]

ENGINEERING BRICKS ("CLINKER" BRICKS)

These are essentially carefully made clay bricks which have been fired to a temperature of 1200°–1300° C. The bonding is in large part iron oxide, which accounts for the blue or red colour. The iron-bearing clay, or mixture of clay and iron oxide, is fired in a reducing atmosphere to produce ferrous oxide. Ferrous compounds with the aluminium silicates form low-melting eutectics, and a dense non-porous brick is obtained at a relatively low firing temperature. Reaction is accompanied by a gradual change from red to blue, though very prolonged firing is necessary for a completely blue brick. The outer skin of the brick may reoxidise on cooling, and as a result the final colour is mottled or "brindled". This is not important, except for ornamental building, but thorough vitrification means strength in the finished brick. It also means low porosity, and a strong brick is often specified because it is not susceptible to frost or water damage. A deep-red heart section, under a blue outer layer, is an indication of rather light firing and possibly of high porosity.

Specifications[4] for these engineering bricks call for a crushing strength of not less than 7000 lb./sq. in. (Grade A 10,000) and a porosity of less than 7% (Grade A 4·7%). The composition is not in any way defined, and it is probable that, as with ordinary building bricks, the chemical make-up varies widely. A typical "Staffordshire blue brick" was made up from

$$SiO_2\ 70\%,\ Al_2O_3\ 20\%,\ Fe_2O_3\ 8\%,\ CaO,\ etc.,\ 2\%$$

This is very similar to the mixture for fully acid-resistant stoneware (below) and probably the only real difference lies in the degree of vitrification and consequent lack of porosity.

As a result, these bricks, which have been developed primarily for all reliable load-bearing work, can be used in a variety of mildly corrosive conditions. Thus a blue-brick floor, laid in asphalt, has given excellent service over many years in an ammonium sulphate plant where spillage of both acid and concentrated salt solution is almost inevitable. Foundations, preferably laid with alumina cement, are proof against all normal soil seepage, and large drainage sewers are built in the same way. An engineering brick construction is the usual basis on which large acid tanks in acid-resisting tile are built. It is not desirable, however, to make the actual surfaces which meet strongly corrosive substances in anything but a specific acid-resisting body.

VITREOUS TILES

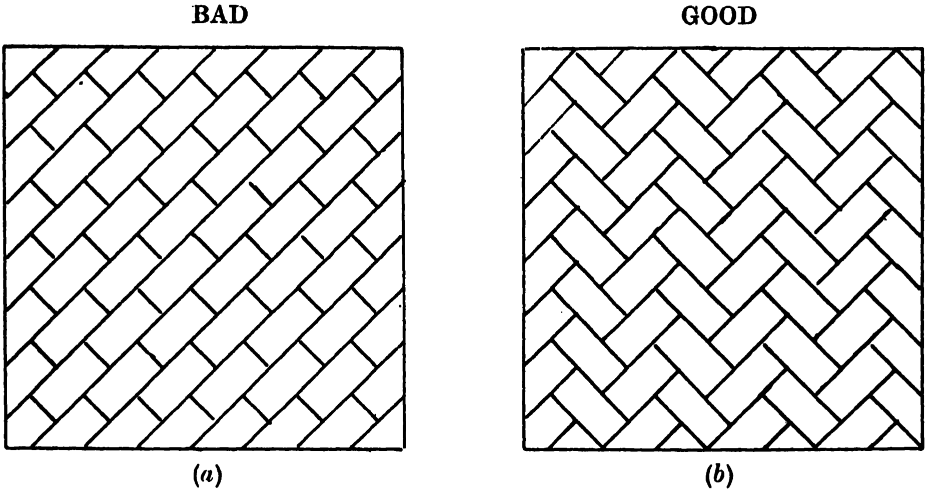
These are the flooring counterpart of engineering brick walls, and are the most common form of floor for all types of chemical plant. Their characteristics have not been so closely specified,[5] while a greater range in size is available. Tiles of up to 12 in. square and 2 in. thick have been used for flooring, though criticised[6] as apt to warp in firing. Thus, though the number of joints is reduced, pools of liquid may form on a floor, which should be as well drained as possible. A smaller and thinner tile can give a more level floor, with less weight on the main beam supports.

Chemical plant floors must be expected to stand up to a good deal of rough usage. As a typical case, consider the floor around a filter press, which will be subject to spillage of liquor and solid, followed by the passage of wheeled trucks carrying the solid cake away. Workmen in heavy boots, handling tools of various kinds, are also about the press at all times. In these circumstances it is almost inevitable that stoneware tiles will crack and chip, no matter how carefully laid. The material under the tiling will be exposed, and any bulky corrosion products will force the tiling up, thus spreading the damaged area. In nearly all modern buildings the original floor structure is in concrete, and tiles should not be laid directly on to this surface. There should be some form of reasonably resistant interlayer, the nature of which is determined by the chemicals being handled. For all aqueous solutions, asphalt is the cheapest and simplest tile base; it should be laid on the concrete in two or more thin layers with all joints "broken" (i.e. not superimposed). If a tarred paper cover is put down first, the asphalt can be taken up very easily for repair without damaging the concrete below. Bituminous roofing felt is a substitute for the asphalt, and can easily be laid by unskilled workers, but such usage would appear to be only a temporary expedient. The German "Kerasolith" process appears to be a combination of asphalt and felt layers, which can hardly be applied so easily to corners or irregular surfaces as the hot fluid asphalt.

Rubber sheeting as an underlayer will have the advantages of resiliency and strength, while the tiles can be sealed to the rubber with a latex cement (Chapter XIV). A floor of this kind is particularly suitable for fine-chemical works where dust is undesirable and hydrochloric acid spillage is possible. The rubber will be laid in sheets of about $\frac{1}{8}$ in. in thickness, and cemented together into a single cover before laying the tiles. Polythene or polyvinyl chloride sheeting can be substituted for the rubber, and is definitely more resistant to a wide range of chemicals, but does not give good adherence between tiles and lining. As the sheets used are very thin—less than 0·01 in.—it is necessary to finish the concrete surfaces below to a smooth polished surface with neat cement.[7] A sheeting made from furane resin and glass fibre has also been suggested, which has the advantage that the tiles can be cemented into place with the corresponding furane resin cement. Lead was sometimes used in the days of its abundance, but it is now relatively expensive, liable to attack by the underlying concrete, and so weak that thick layers would be necessary.

All these undercoatings, with the possible exception of the last two, are thermoplastic, and the floor should be protected against too much heat. Steam- or gas-heated plant should not be too near, and even generous hosing down with hot water can cause local failure. The tiles are normally thick enough to protect the underlayer, but some caution is necessary.

The tiles should be laid on the undercoat with lightly cemented narrow joints, choosing some resilient bond such as sulphur cement. The tiling should not be arranged to give long straight joints as in Fig. XV–3*a*, but in "herringbone" form (3*b*). Such an arrangement calls for accurately cut tiles and very thin seams, but offers better resistance to all types of wear and gives a less slippery surface when wet.[6] If oil or grease spillage is expected, tiles with a specially roughened surface should be used, and, of course, asphalt-based joints should be scrupulously avoided. Large floor areas laid in close tiling need some form of expansion joint, generally a pair of metal strips laid an inch apart and filled with soft asphalt or some similar material. If the flooring is to be subject to considerable changes of temperature and reasonably light wear, the tiles can be laid into, e.g., rubber latex cement, leaving ¼-in. gaps, and these wide seams are then "pointed" with asphalt or sulphur cement, pouring or trowelling to give a level surface. All floors should be laid with a definite slope for drainage and easy washing, as already indicated with asphalt.



(a) (b)

FIG. XV-3.—A.R. TILE FLOORINGS.

ACID-RESISTING BRICKWORK

The line of demarcation between this form of vitrified stoneware and the engineering bricks or tiles described above is not clearly marked. The composition of three typical "A.R." bricks, set out in Table XV-2, does not differ widely from that of ordinary brick, and the only real difference appears to be in the degree of porosity.

TABLE XV-2

	Brick A	Brick B	Brick C
SiO_2 . . .	61·5	79·1	82·8
Al_2O_3. . .	24·8	15·2	11·9
Fe_2O_3 . .	6·9	3·5	0·5
MgO, CaO, etc. .	2·7	1·5	—
	Porosity less than 4% and generally less than 2%.		

effect of the brick wall. Such protection is common to all plants utilising A.R. brick, and it is possible to design plant in which sulphuric acid of over 90% H_2SO_4 is boiled without affecting a thermoplastic undercoat. The life of brickwork in a Glover tower is prolonged. It is generally necessary to dismantle after ten years or so because of dust deposition, but more harm is done to the bricks in dismantling than in the whole working life of the tower.

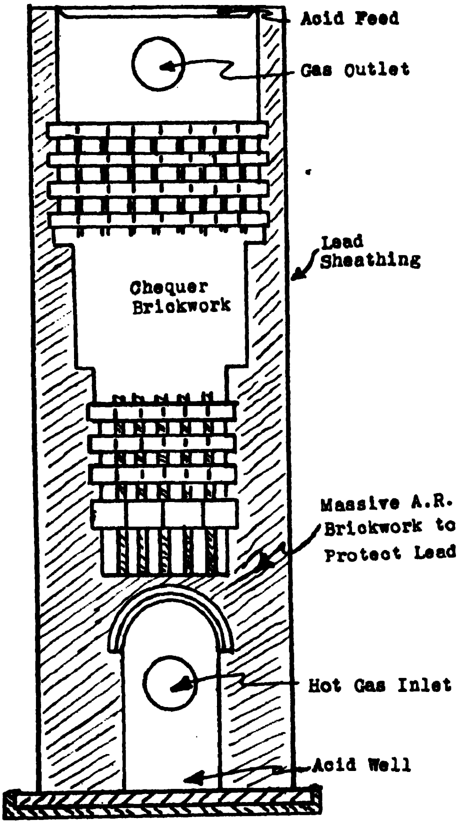


FIG. XV–4.—ACID RESISTING BRICKWORK FOR GLOVER TOWER. (30 ft. high, 9 ft. sq.)

Large tanks for "pickling" steel or cast iron to remove oxide films, a process carried out with mixtures of sulphuric, nitric, and hydrochloric acids, are almost invariably lined with A.R. tiles and bricks. The tiles can be obtained in sections as large as 24 in. by 9 in., normally about 1 in. in thickness, with grooved or tongued edges, carefully squared for thin even joints. Rounded shapes for tank corners and edges are available, as shown in Fig. XV–5*a*. The completed tank must stand up to rough mechanical usage, with heavy metal masses bumping against sides and base, but the tiles answer very well, and some dipping tanks have been in constant use for more than twenty years. As tanks for this work can be quite large (up to 30 ft. long, 10 ft. wide and 6 ft. deep) it is out of the question to build from anything but relatively inexpensive materials. Good-quality A.R. tiles will not cost more than £15 per ton and are easily the cheapest form of acid-resisting material available. The one unfortunate shortcoming is the low thermal conductivity, which at most will be about 0·8 B.Th.U./(sq. ft.)(hr.)(° F. per ft.). Heating a tank from the outside is more or less impossible, and some form of immersed heating coil is required for high temperatures. Tiled linings can be put into metal plant, as shown in Fig. XV–5*b*.

Resistance to Corrosion

Properly made A.R. brickwork will stand up to any concentration of sulphuric, nitric, or hydrochloric acid at any possible liquid temperature. The shapes will be equally resistant to salt solutions or to caustic alkalies of under 10% concentration. There is clearly no purpose to be served in using A.R. tiles for this last, and any more concentrated solutions should be avoided. Hydrofluoric acid attacks the brick surface readily, liberating toxic gases, and obviously cannot be contained in such plant. Phosphoric acid, when cold, has little or no action on a practically nonporous brick, but when hot it can form a complex glass of mixed oxides and low melting-point. Chlorine, bromine, and iodine have no action, either wet or dry, and one important application in organic preparations is the lining of reaction vessels for brominations and the like. The surface is noncatalytic, and will not decompose unstable chemicals

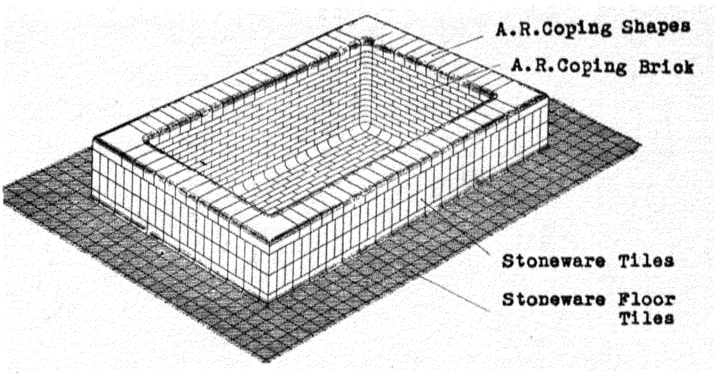


FIG. XV–5*a*.—ACID TANK FOR METAL TREATMENT.
(*Courtesy of Hathernware, Ltd.*)

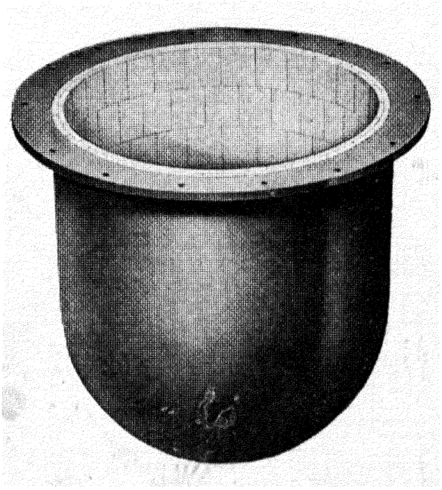


FIG. XV–5*b*.—TILE-LINED CAST-IRON REACTION VESSEL.
(*Courtesy of Doulton & Co.*)

such as hydrogen peroxide. A carefully lined tank is an alternative to enamelled steel for many surface-sensitive chemical operations, and has the advantage that there are no restrictions on size. The weak point in such lined tanks is the joint between sections, which should always be as thin as possible. No brick section should be roughly chipped to fit and the shortcomings disguised with cement; any odd hole should be filled with a brick shape that has been cut properly to form. The various cements available have already been described in the two preceding chapters.

CHEMICAL STONEWARE

This is the final stage in vitrification, and almost without porosity. Suitable clay mixtures are fired to about 1300°–1400°, the higher temperatures with a pure kaolin giving the characteristic porcelain structure. Chemical stoneware made in this way must be distinguished from the common earthenware used for sinks, drains, and general sanitary ware. This is resistant mainly by virtue of a glazed covering, and the body underneath can be porous and even quite reactive. Such products should not be used in chemical plant, except for such purposes as rainwater drains. A kaolin clay designed for porcelain will have a composition corresponding to 55% silica, 45% alumina, with practically no other ingredients, but the lower melting body for general stoneware contains more silica and up to 2% of other oxides. Again the exact composition will be of little importance compared to the low porosity (below 0·5%) and even texture. The porosity of porcelain is immeasurably small, and thorough firing has given material of high crushing strength. Unfortunately the thermal conductivity is no higher than that of A.R. brick, though special high-conductivity forms incorporating silicon carbide have been made.[9] Characteristic properties for the normal stoneware are set out in Table XV–3

TABLE XV–3

Specific Gravity	2·5–2·6
Porosity	Less than 0·5
Tensile Strength	1000–2000 lb./sq. in.
Compressive Strength	40,000–60,000 lb./sq. in.
Thermal Conductivity	0·8–1·0 B.Th.U./(sq. ft.)(hr.)(° F./ft.)
Linear Expansion Coefficient	$4{\cdot}5 \times 10^{-6}$ in./(in.)(° C.)

The method of manufacture sets limits to plant size, at any rate for single pieces. Cylindrical sections have been made up to 6 ft. in diameter and 7 ft. long, but this represents an absolute ceiling, and more usual limits are about 4 ft. by 4 ft. Problems of shrinkage or even firing will probably prevent the manufacture of any piece with a larger diameter than about 6 ft.

A stoneware vessel will not normally be put under any real mechanical stress, but may have to deal with thermal shock. Some grades of stoneware can be made to withstand sudden immersion in boiling water, but ideally a maximum temperature difference between fluid and stoneware of about 50° should be set. Special shock resistant grades of higher porosity are available with coefficients of linear expansion as low as $1{\cdot}5 \times 10^{-6}$. The surface hardness is very high, as shown by the use of ceramic tips for high-speed cutting tools, and the resistance to abrasion is unaffected by such factors as stress corrosion. A stoneware sheath on a centrifugal pump shaft, passing through a packed gland, will give years of wear in most unpleasant conditions.

The "classical" form of nitric fume absorber is a tower made up from stoneware sections, with spigot and faucet joints packed in acid-resisting putty. Dilute nitric acid circulates in the tower, pumped to the top by an air-lift, with a stone footpiece and glass conduits. A set of six such towers, with the acid flowing counter-current to the fume in series, will reduce nitric fume loss to a negligible figure while working up to a 50% HNO_3 solution. They have been commonplace in acid works for nearly half a century, but are still being erected as the most economic form of recovery unit. The packing is of stoneware "Raschig rings", available in sizes from ½ in. up to 6 in. in diameter and length. These rings stand a very considerable load applied across the cylinder axis, and when "random packed" the load on a single ring at the base of a 10-ft. section is claimed by manufacturers to be less than one-tenth of the crushing strength. It is preferable, however, to arrange for some support, such as a perforated reinforced plate (Fig. XV–6), which will also act as a redistributor of the fluid flows. Partition (Lessing) rings are stronger and a trifle more expensive, while many other forms of stoneware shape are available (Fig. XV–7).

A more severe test of the material is applied in the operation of denitration or nitric acid concentration towers. A stream of H_2SO_4–HNO_3 trickling down the packed tower is met by an upward current of steam, changing gradually to nitric acid vapour, with temperatures which may reach 200° C. The stoneware shell is built up in sections as before, but the flanged ring ends are ground to a close fit and the final joint is made by a thin silicate cement. The built-up tower is sheathed in steel, with an intervening layer of acid-resisting cement, while the outlet pipes are made in high-silicon iron. The packing of an acid-concentration tower is generally made from quartz chips or pebbles, while each joint is protected by a drip-ring

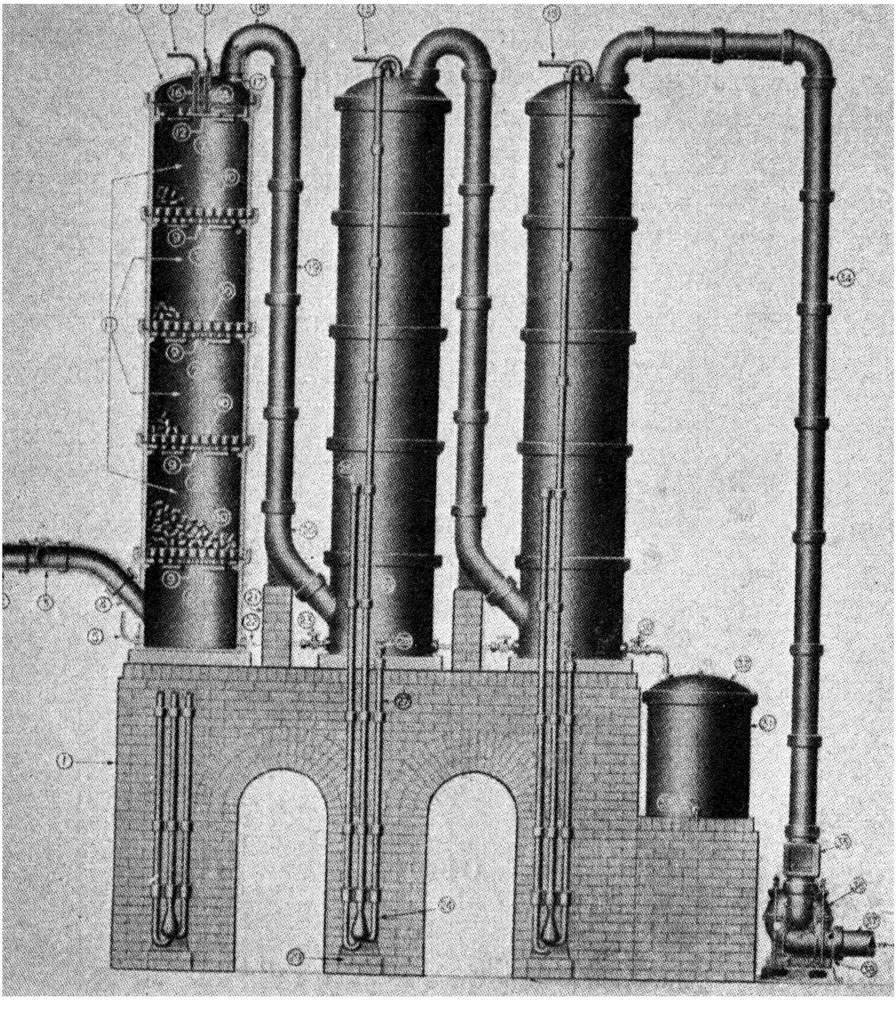


FIG. XV–6.—STONEWARE ABSORPTION TOWERS.

(*Courtesy of Hathernware, Ltd.*)

section at the inner edge of the flange (Fig. XV–8). Special porcelain packings might be used, as this could stand up to boiling concentrated sulphuric acid, but apparently the extra cost is not worth while. Porcelain trays and bubble caps were used in the old

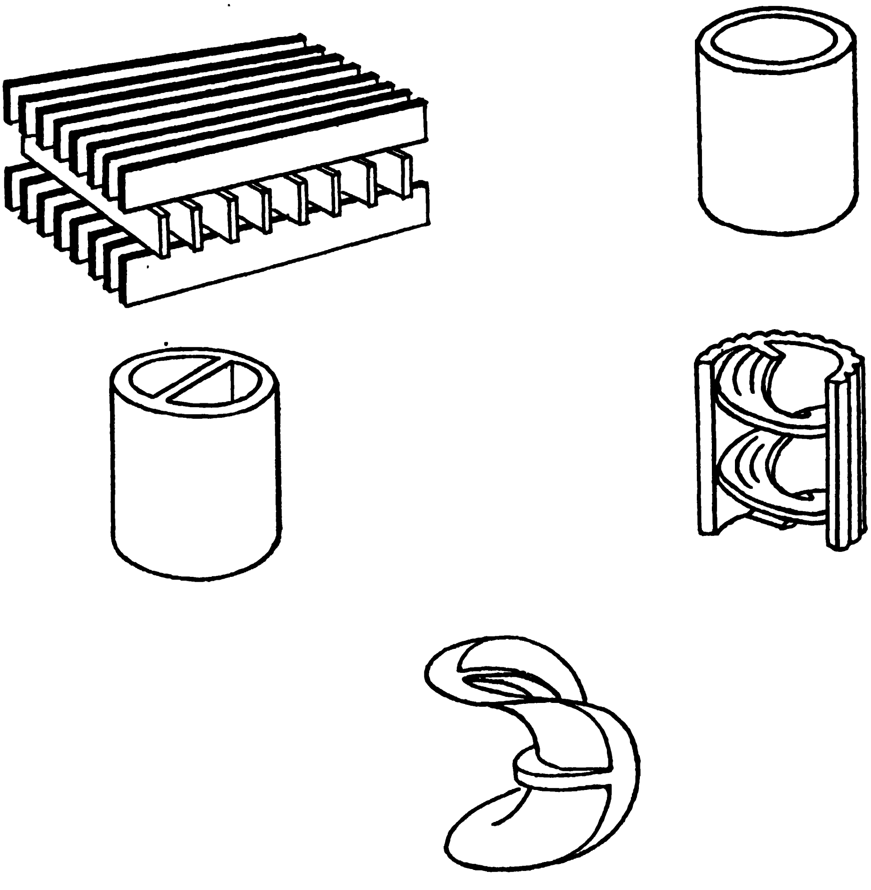


Fig. XV–7.—Stoneware Shapes for Absorption Tower Packings.

“Kessler” sulphuric acid concentrator, but these plants are no longer being built.

Stoneware containers can be obtained in sizes up to 4 ft. in diameter and 8 ft. high, as in Fig. XV–9. They can be fitted with stoneware taps, made with a ground spigot to match a socket in the bottle. A pressure-lubricated form, in which the grease lifts the plug of the tap from its seat, is well worth the extra cost when using stoneware in this way, and as a further precaution the whole tap is sometimes sheathed in steel—an “armoured” tap. Centrifugal pumps are available in which both impeller and casing are of stone; impeller and casing can be shaped into complicated forms before firing and present no real problem. The major difficulty in manufacture is to attach the impeller to a steel shaft in such a way that no corrosive agent is admitted to the metal. If acid penetrates to the shaft, gas evolution or bulky corrosion products burst the stone impeller. Thermosetting resin cements give reasonable satisfaction, but an occasional failure still occurs. Pumps have been made with a capacity of 800 gall. per minute, delivering to a 120-ft. head—the largest output likely to be required when dealing with strongly corrosive solutions.

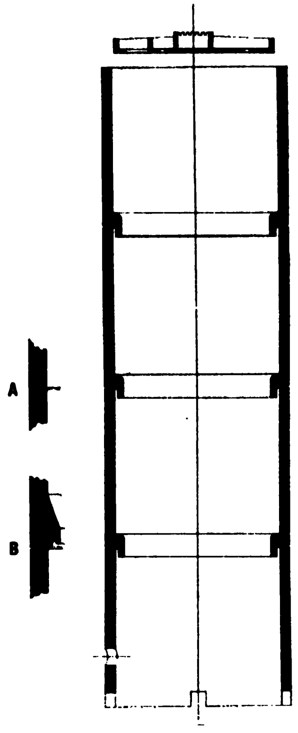


FIG. XV-8.—JOINTS IN STONEWARE TOWER (A) BUTT JOINT (B) DRIP RING (C) INTERNAL FLANGE.

(*Courtesy of Doulton & Co.*)

Fans for handling acid gases can be obtained with impeller diameters of 33 in., running at 1200 r.p.m. They are heavy and clumsy and it is doubtful if the use of stoneware is justified in this case. Steel sheathed in some form of protective covering, or a special metal, might be a sounder proposition. On the other hand, stone ejectors for vacuum pumping are widely used; the erosive action of high-velocity steam jets, combined with a variety of acid vapours, can destroy most metals, but leaves stoneware quite untouched. It is a pity that the interstage condensers of a multistage ejector system cannot be made in stoneware, but the normal conductivity is much too low, even if fabrication difficulties did not arise.

Although the ultimate tensile strength is low, the normal pipe has a thick enough wall to withstand pressures of the order of one atmosphere. For fume ducts, in which the variations of pressure are some 30 in. water-gauge, long fume mains in any well-made stone are cheap and efficient. They may need expansion joints, which are readily improvised from a wider section of piping, and have to be slung from an overhead gantry or laid in a wooden trough. Joints are usually of the spigot and faucet type, with soft putty packing, but flanged joints, asbestos gaskets, and steel reinforcing give a joint which will stand up to as much as 15 lb./sq. in. without difficulty.[12] Earthenware pipe, as used for drains and sewers, is not acid-resistant except by virtue of a glazed surface. The glaze—a borosilicate glass at best—is moderately resistant, but beneath this layer the body is soft and porous. Even high-grade sanitary ware is made from the more highly vitrified stoneware, and pipes for acid fume should have equally resistant properties. Stone pipes for liquids are uncommon, except in drainage work, although some regulations for dimensions have been made.[11]

The introduction of rubber and more recently synthetic resin has diminished the importance of stone in making or storing hydrochloric acid. It is more usual nowadays to make the HCl by burning chlorine in hydrogen, but many of the older salt-cake pans are still at work, and both produce an acid gas which must be absorbed in water. The "Cellarius" absorber devised for this purpose was made in stone, as shown in Fig. XV–10. Modern plant may replace these with silica or graphite absorbers, but the cost will be considerably higher, despite the greater compactness of the unit. Acid resistance is complete at these lower temperatures, and breakage can only occur through mechanical shock.

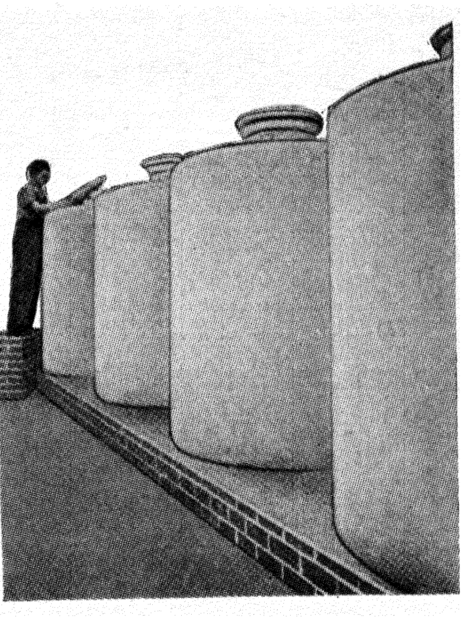


FIG. XV–9.—LARGE STONEWARE JARS. (*Courtesy of Hathernware, Ltd.*)

The only acids for which this material cannot be used are hydrofluoric and hot concentrated phosphoric solutions. Iodine and bromine, wet or dry, have no action, and there is no possibility of metallic contamination or catalytic action when handling delicate chemicals. Resistance to alkalies is poor, and even a weak solution of caustic soda can roughen the surface, but there is clearly no need to use stoneware for such reagents.

The real advantage of stoneware over other corrosion-resistant materials lies in the price. Only a very complicated form would cost more than 8*d.* per pound, and a more usual figure would be about 2*d.*—£20 per ton. Of course, this is offset by the weight of typical sections, but a given plant section is usually much cheaper than a corresponding unit in glass or fused silica. Although the plant should have an indefinite life if rightly used, accident or thermal shock terminates a relatively short life as a rule, while the scrap value of broken stoneware is something less than nothing.

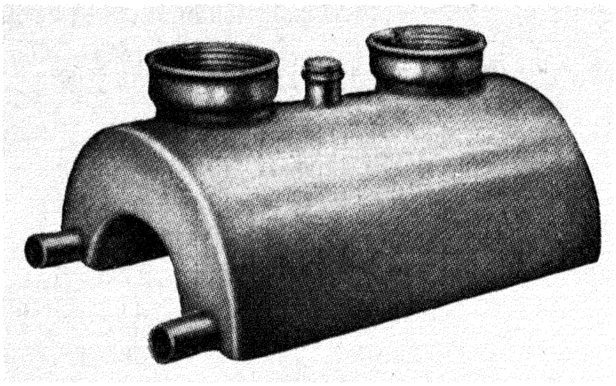


FIG. XV-10.—"CELLARIUS" ABSORBER IN STONEWARE.
(*Courtesy of Doulton & Co.*)

REFERENCES

1. Symposium, *Chem. Engng. Progr.*, 1951, **47**, pp. 277, 339, 341, 385.
2. National Building Studies Bulletin No. 1, Clay Bricks, H.M.S.O., 1948.
3. National Building Studies Bulletin No. 4, Sandlime and Concrete Building Shapes, H.M.S.O., 1948.
4. B.S. 1301 (1946).
5. B.S. 1286 (1945).
6. Marsden, L., "Materials of Construction", p. 42.
7. Himsworth, F. R., *Chem. and Ind.*, 1950, 55.
8. B.S. 784 (1938).
9. See, e.g., Kingsbury, P. C., *Trans. Amer. Inst. Chem. Eng.*, 1940, **36**, 439.
10. B.S. 1257 (1945).
11. B.S. 1634 (1950)
12. Anon., *Ind. Chem.*, 1953, **29**, 415.

two. A typical curve showing behaviour of a chrom-magnesite brick under load is shown in Fig. XVI–1.

THERMAL EXPANSION

A solid which is built up into a complicated form when cold and then heated up to 1500° C. or thereby should clearly not possess a high coefficient of thermal expansion. Even if a single brick is uniformly heated, the structure of which it forms part may not expand in the same way, and a stress is imposed at all joints. Again, the heating is faster on the furnace side than on the other face of the refractory structure, and differential expansion can develop enough force to fracture the brick or split off the hotter fragments—"spalling" of bricks. All this is quite apart from the fact that certain minerals can exist in two or more forms, with varying density and temperature stability. Despite careful choice of refractory, it can usually be expected that a reversible thermal expansion of at least 1 × 10^{-5} (in./in. ° C.) will occur, giving a linear expansion of 1% as a furnace setting is heated up to 1000° from the cold. Many large industrial furnaces are over 100 ft. long, and the whole of the interior will be at temperatures above this level. It is impossible to heat and cool these furnaces like a reaction vessel of normal type, and the

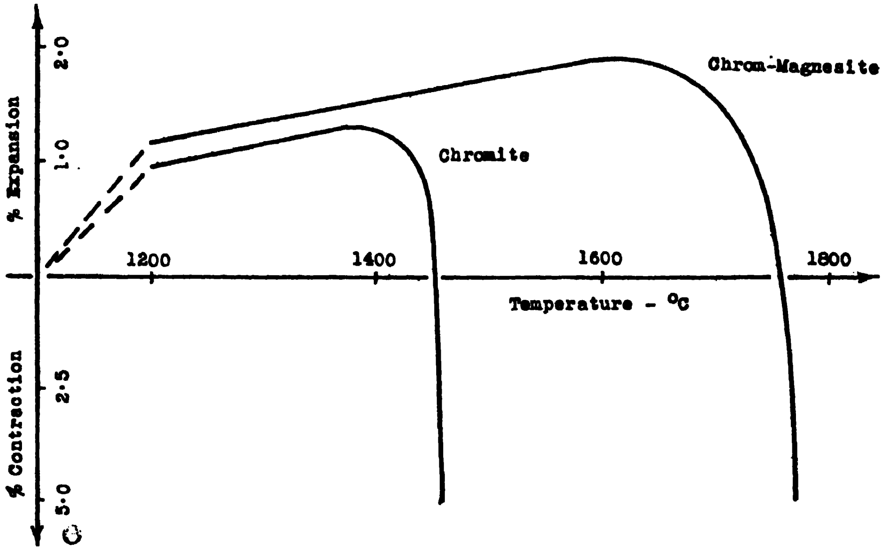


Fig. XVI–1.—Refractoriness Under Load.
Temperature Rising at 10°/Min.

specific heat, and ϱ is the density, all in self-consistent units. Whenever a mass of refractory material is to be heated and cooled at fairly frequent intervals, it is desirable that the diffusivity shall be as high as possible, if only from the viewpoint of thermal economy. This point is brought out in Fig. XVI–2, which compares the performance of carborundum and firebrick refractories. The effect on spalling may be masked by other and more potent features such as the thermal expansion, but high diffusivity is normally associated with low spalling figures.

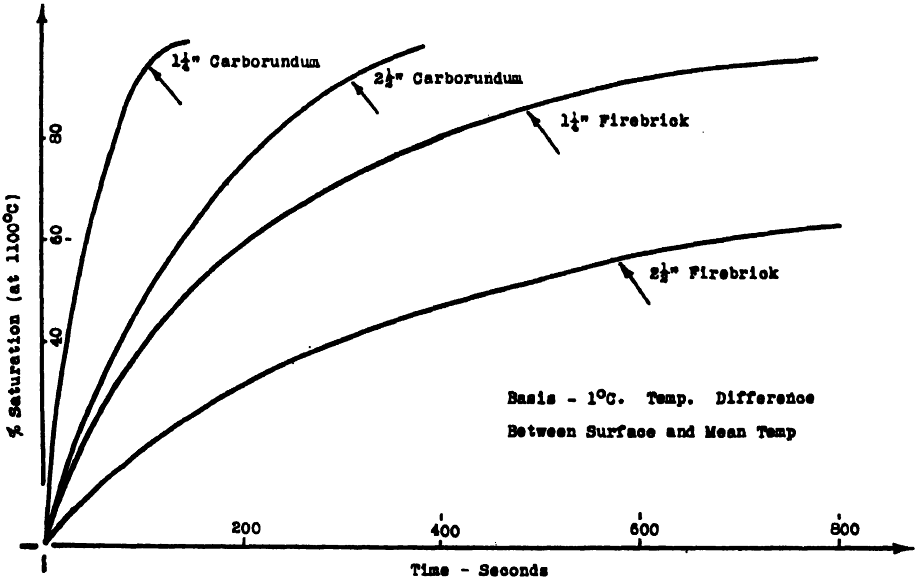


FIG. XVI–2.—HEAT SATURATION CURVES.
(After C. F. Geiger *et. al.*, *Chem. Eng. Prog.*, 1948, **44**, 933)

PERMEABILITY

This is to a large extent a function of the porosity, which can vary enormously, from a negligible figure with solid cast blocks to over 75% with special insulating bricks. As some pores are open to fluid diffusion while others are sealed, the relationship is indirect and some insulating bricks have lower permeabilities than ordinary firebrick. In general, however, high porosity means high permeability, and this in turn implies that the refractory will readily be attacked by gases or molten slags. Carbon monoxide decomposes readily at many solid surfaces between 300° and 700° according to the reaction $2CO \rightarrow C + CO_2$, and the carbon, deposited as a solid, forces the refractory grains apart. Both hydrogen and carbon monoxide, at high temperatures, can reduce silica to silicon monoxide —a volatile product. In fireclay bricks a residue of corundum may be dense enough to check disintegration, but a porous silica brick can almost disappear. Actual permeabilities can vary from 0·01 to 0·50 (ml. of air per second per sq. cm. for 1 cm. water pressure per cm. length), the highest values being commonly found for silica bricks with a porosity of about 30%.

MECHANICAL STRENGTH—ABRASION RESISTANCE

A refractory brick must resist rough handling in process of transport and while a furnace is being built, even though it is never used to resist heavy loads. Resistance to crushing will normally be a measure of the way in which bricks will stand up to such rough treatment. Many silica refractory shapes are particularly fragile, and must be carefully packed for transport. Naturally they will not resist abrasion well, though performance generally improves on prolonged firing and is better at furnace temperature than in the cold. Pure refractory oxides are difficult to bond, and the addition of bonding agents may lower the refractivity to a dangerous degree. As a result of the compromise generally made between this refractoriness and strength, the typical refractory brick will be decidedly weaker than an engineering brick (cf. Chapter XV), with a crushing strength which ranges from 1000 to 5000 lb./sq. in.

MANUFACTURE

This follows the normal rule for brick manufacture in that minerals of suitable composition are rough-ground and wetted, shaped into blocks and heated to sintering temperature. As the firing temperature is higher, problems of shrinkage and distortion are more marked than with ordinary brick, and a large proportion of prefired fireclay—"grog"—is always incorporated into the mixture. It is possible to melt certain mixtures completely, using electric furnaces and temperatures of the order of 1800°, and the melt can then be cast into solid blocks, but the technique is very expensive. Grog alone can be ground to form a fine slurry, and then "slip cast" by running into plaster-of-Paris moulds. The shapes so obtained are tough and need only a light firing to convert to a usable firebrick shape. Refractory concrete, made from crushed firebrick and high-alumina cement, has already been mentioned increasing basicity, can only be taken as an approximate guide to behaviour.

TABLE XVI–1*

Description or Title	Composition (% by weight)						Refractoriness under Load (28 lb./sq. in) ° C.	Reversible Thermal Expansion 20°–1000° C.
	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Other Const.		
High-Silica Brick	95–98	1	1		1		1650	1·3 (1·2 to 600°)
Siliceous Fireclay	70	25–30	1		1		1380	0·60
Normal Fire-clay	50	35–40	2		6–7 Inc. Ti		1550	0·75
Kaolin	52	45	0·5		1	TiO_2 1·5	1620	0·57
Sillimanite	38	59			2		1700	0·58
Zircon-Silica	32					ZrO_2 66	1700	0·41
High Alumina (Mullite)	27	69			3		1700	0·7
Carborundum	7	4				SiC 88–90	1700	0·48
Soapstone	56	4		32	7		1400	
Carbon Block	Almost pure Carbon						>1800	0·65
Chromite Block	4–6	16–20	1–2	13–20	12–15	Cr_2O_3 36–40	1450	0·85
Chrom-Magnesite	4–6	14–20		38–40	10–14	28–30	1750	1·0
Forsterite	38	2		52	7		1700	1·0
Stabilised Dolomite	13	2	39	41	3		1700	1·3
Dolomite	4	2	49	39	2		1600	
Magnesite	2–3	5–6	1	88–96	2–3		1570	1·1

* Generally after Partridge and Barratt, *loc. cit.*

SILICA BRICK

High-silica refractories should contain as much of the pure SiO_2 as possible. The low-melting eutectic with Al_2O_3, an obvious additive, only contains 5·5% of alumina, and traces of alkali can produce liquids at temperatures below 1000°. Nevertheless, unless the extreme step of melting the whole material is taken, some bonding material must be incorporated into the raw brick mix. This additive will modify the characteristic changes of SiO_2 with temperature, but the finished refractory must exhibit the general properties of its principal constituent. Silica can exist in three crystalline forms, and each of these in turn has two possible modifications, while vitreous silica can also exist—though always unstable. These forms and the temperature ranges in which they tend to form are set out in Table XVI–2.

TABLE XVI–2

Form	Temperature of α—β Transformation (° C.)	Temperature Range for Stability (° C.)
Quartz . . .	573	Up to 870
Tridymite . . .	115–165 B_1 B_2	870–1470
Cristobalite . . .	200–275	1470–Melting-point

It will be seen that tridymite and cristobalite can persist at quite low temperatures, and rates of transformation between the three forms are always low, though they may be increased by the presence of metallic oxides such as lime. On the other hand, $\alpha \rightleftharpoons \beta$ changes are rapid, putting much more strain in a refractory shape than the slower intercrystalline modifications. The expansion curves caused by these $\alpha \rightleftharpoons \beta$ changes, combined with normal thermal growth and shown in Fig. XVI–3, indicate the need for very careful treatment of any silica refractories on heating from ordinary temperatures up to 600°. The worst constituent of the brick appears to be cristobalite, and the least troublesome tridymite, but it is not possible to obtain a purely tridymitic grog for firebrick manufacture. Quartz has a smaller expansion than cristobalite in its α → β transformation, but

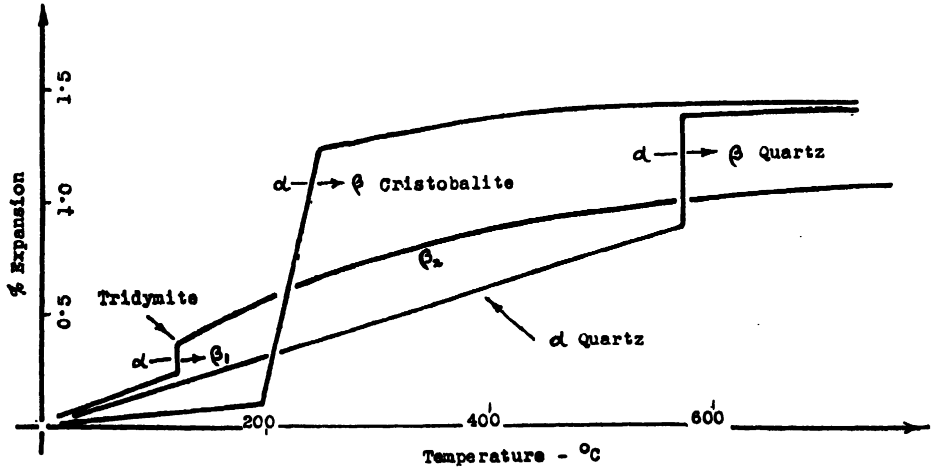


FIG. XVI–3.—STRUCTURAL CHANGES IN SILICA.

TABLE XVI-3

Form	Specific Gravity	
	α Modification at 0°	β Modification at 600°
Quartz	2·65	2·53
Tridymite . . .	2·28	2·19
Cristobalite . . .	2·33	2·20

has a much higher density, as shown in Table XVI-3. A change from α quartz at 0° to β tridymite at 600° means a volume change of no less than 20%, or a linear expansion of more than ¾ in. per foot. Clearly the bulk of a brick must be made from prefired material, and with proper precautions it is possible to obtain a refractory shape with over 90% of the free silica as tridymite (manufacturer's claim). There is still a marked expansion over the critical range up to 600°, as will be seen from the curves of Fig. XVI-4. The heating of any setting made from silica brick must therefore be carried out with extreme care until the temperature exceeds 600°, and such refractories are unsuitable for any furnace which must be heated and cooled at frequent intervals. This is regrettable in that silica brick is the cheapest material for reliable use under load at all temperatures up to 1600°, and shows practically no volume change right from 1000° up to the fairly sharp failure point (Fig. XVI-5). Thermal "shock" in this range is almost harmless to silica brick. If a complete setting is to be heated up to 1400° and held there for long periods, as with a coke oven, then silica brick is almost always

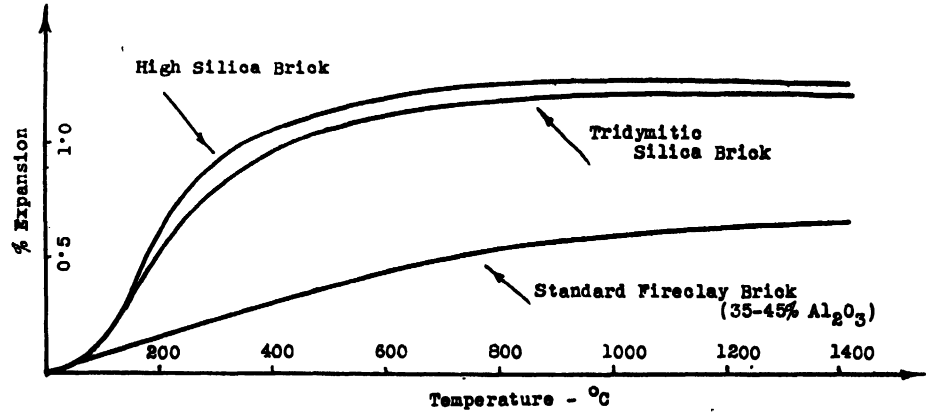


FIG. XVI-4.—THERMAL EXPANSION OF REFRACTORY BRICKS.

used. It was the custom to lay the bricks with blocks of cardboard or felt, ½ in. in thickness, at each 2 to 3 ft. while building a setting, but this practice has now been abandoned and sufficient room left for the brickwork mass to expand as a whole on heating up to working temperature. Values for the specific heat and thermal conductivity of silica brick are set out in Fig. XVI–8 and 9, but it must be remembered that no absolute figure for *all* silica bricks can possibly be specified. This is particularly true of the conductivity, which can be greatly modified by porosity. Diffusivity values will range from 0·0035 to 0·0050 over the temperatures 6000°–1300°.

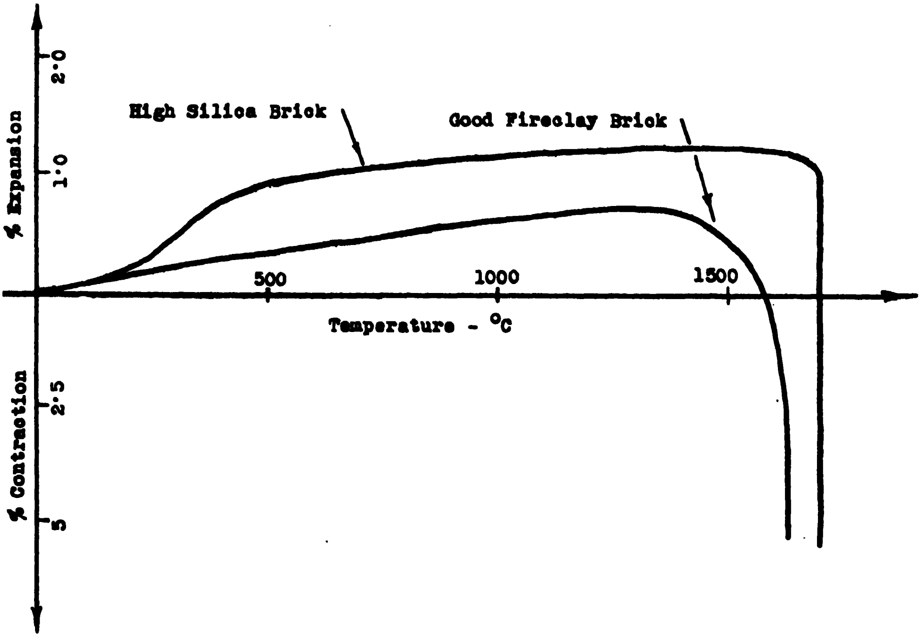


FIG. XVI–5.—REFRACTORINESS UNDER LOAD.
(Rate of Heating—10° C./Min.)

Corrosion Effects

Silica brick reacts easily with all metallic oxides to form relatively low-melting fluxes. It cannot be used as a lining for metal ladles in casting work, the hearths of smelting furnaces, or the high-temperature zone of cement kilns. Alkali vapours, from glass melting, attack a silica-brick ceiling rapidly, and coal with high-sodium-content ash should not be used in producers which are to heat a furnace setting. Molten glass is very destructive to all acidic refractories, and roasting furnaces for soda redemption, as in paper manufacture, cannot be lined in silica brick. In a strongly reducing atmosphere free silica can be volatilised as the monoxide, but any combination with alumina, as in mullite (see below), is much less easily reduced. As might be expected, acidic gases have little or no action. A combustion chamber for hydrogen–chlorine, too large for Vitreosil work (Chapter XVII), can be built up in silica shapes, while silicon tetrachloride is made by passing chlorine into red-hot silicon, contained in a vessel of the same silica-brick construction.

FIRECLAY BRICKS

The properties of these bricks are best understood by reference to the phase diagram for SiO_2–Al_2O_3 (Fig. XVI–6). It will be seen that for all except the very high alumina and silica compositions the characteristic solid phase is mullite (72% Al_2O_3) in equilibrium with a melt containing more silica. A fireclay brick is a mixture of various clays which only slowly attain complete thermal equilibrium. When heated up to some initial melting-point, the mixture will partially fuse, and then deposit mullite crystals from a silica-rich liquid. Even a thoroughly prefired brick will contain traces of the lowest-melting eutectic, unless it has actually been made from mullite. As a result, the behaviour of fireclay shapes on heating can be represented as in Fig. XVI–7, in which the proportion of liquid formed is plotted against the temperature. All fireclays, with the

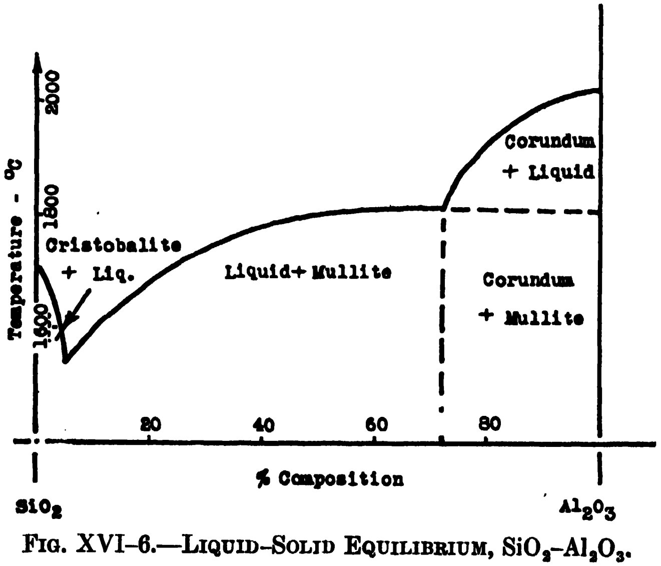


FIG. XVI–6.—LIQUID–SOLID EQUILIBRIUM, SiO_2–Al_2O_3.

exception of pure mullite, will start to melt at about 1500°, but can take loads by virtue of the solid residue. A poor fireclay, with alumina content below 25%, and other fluxing agents present, will have 60% of the brick in a molten form at 1550°, and the effective strength will be virtually nil. A kaolin, with only 25–35% liquid at the same temperature, still has some load-bearing properties, while a sillimanite composition (63% Al_2O_3) will retain some semblance of shape up to 1700°. Mullite shows no change until the true melting-point is reached at just over 1800°, when the solid decomposes to a mixture of alumina and a 55% Al_2O_3–SiO_2 complex. The characteristic curve of a silica brick is shown for comparison.

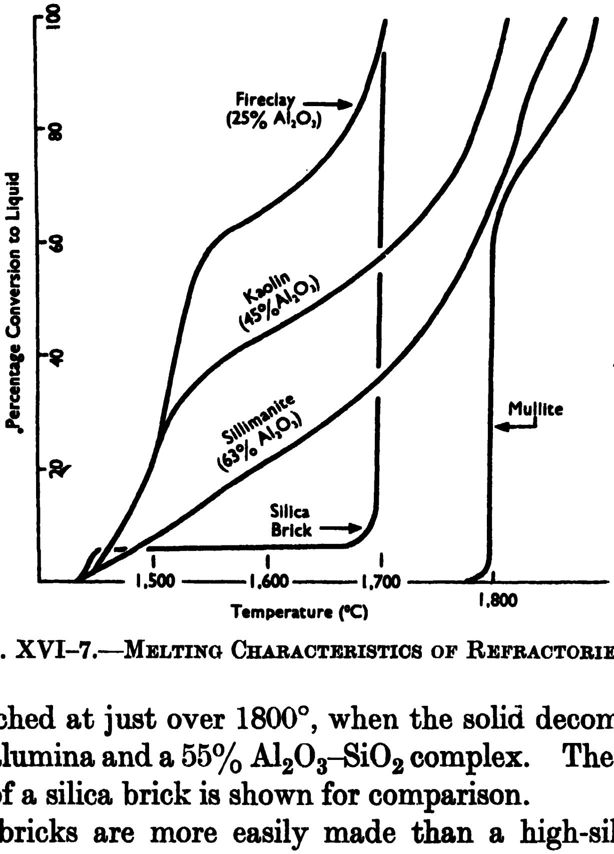


FIG. XVI–7.—MELTING CHARACTERISTICS OF REFRACTORIES.

Fireclay bricks are more easily made than a high-silica shape, and no unfortunate changes in crystalline form occur. The thermal expansion of a normal fireclay brick (Fig. XVI–4) is almost linear from 0° to 1200°, with a total increase of 0·65–0·75% in length, and still smaller figures can be obtained with sillimanite and kaolin compositions. The excessive caution needed when heating silica from 100° to 600° is no longer required, and the bricks, in general, are much stronger. As the percentage of alumina increases, the amount of prefiring required is also extended, while the final shapes are less easy to bond. Mullite bricks are sometimes made by fusing and casting as a solid block, or from graded mullite grog sintered with a minimum of clay. Such methods are expensive, and the finished bricks are only used for special purposes, such as lining the pan of a glass-melting furnace.

The cold crushing strength of a properly made fireclay brick will be little less than that of engineering bricks, and is usually quoted at 4000–5000 lb./sq. in. The specific heat will be almost the same as for silica brick, as shown in Fig. XVI–8, though mullite has a somewhat lower value. The thermal conductivity will vary, of course, with porosity, but is generally lower than that of silica, Fig. XVI–9. Largely as a result of this, the diffusivity of fireclay is about 0·0025 to 0·0035 over the range 600° to 1300°.

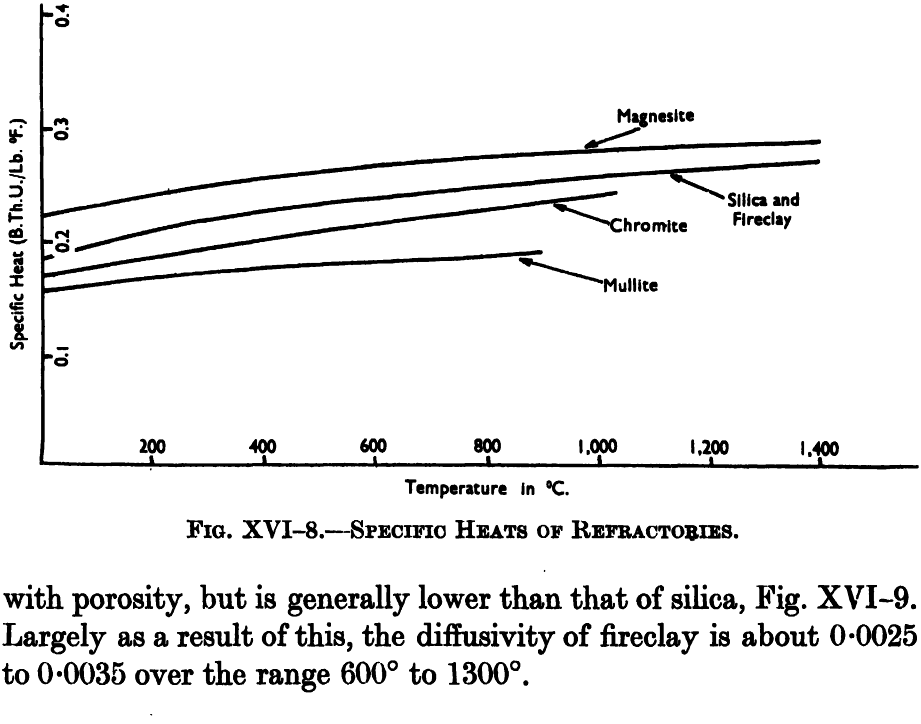


FIG. XVI–8.—SPECIFIC HEATS OF REFRACTORIES.

Corrosion Resistance

As the cheapest and most easily made refractory material, fireclay bricks, containing from 25% to 45% of alumina, are generally used for all furnace construction when the working temperature is below 1400°, and they are much less reactive than the more thermally stable silica. Fireclay is still attacked, however, by molten metal, and alkali vapours can destroy a setting at temperatures above 1000°. All normal boiler settings are made up in firebrick, and the chief virtue of fireclay in this field is that it is not subject to spalling or disintegration on cooling. As the brick shapes are stronger than silica, they are preferred where abrasion is encountered, as in producer linings. Hot-gas mains, carrying producer or water gas, are lined with firebrick of low permeability to check disintegration by deposited carbon. A cement kiln is lined with fireclay brick until the highest temperature levels are reached, when high-alumina or basic bricks take over. Lime kilns do not normally reach a dangerous temperature level and are built in firebrick throughout.

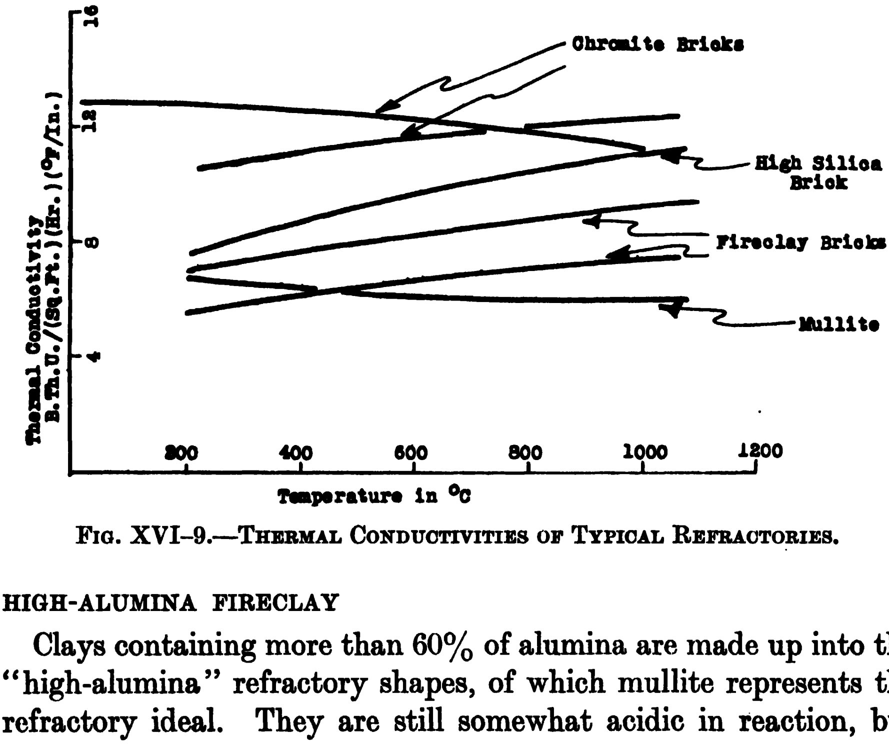


FIG. XVI–9.—THERMAL CONDUCTIVITIES OF TYPICAL REFRACTORIES.

HIGH-ALUMINA FIRECLAY

Clays containing more than 60% of alumina are made up into the "high-alumina" refractory shapes, of which mullite represents the refractory ideal. They are still somewhat acidic in reaction, but are more refractive than the ordinary fireclay and slightly less reactive. It is difficult to make up mullite shapes, and a sillimanite composition is more common. Many cement kilns are lined throughout in sillimanite brick, while a similar composition has been recommended for lime and dolomite roasting furnaces. Mullite blocks can justify their high cost in the lining of molten glass tanks or for very high temperatures in reducing atmospheres. The "pebbles" of pebble heaters, used in moving-bed regenerators, are commonly made of mullite grog sintered with a clay bond that gives mullite on firing.

A "corundum" brick, with 88–92% of Al_2O_3, can be made by the same methods as with mullite. Such bricks are uncommon, and apt to fail by spalling, despite a high thermal conductivity (up to 24 B.Th.U., etc., has been claimed). The resistance to alkaline ash is good, and corundum bricks have been used for lining oil-fired furnaces where the oil is contaminated with sodium chloride (sea water).

ZIRCON AND ZIRCONIA

Zirconium silicate ($ZrSiO_4$) is a naturally occurring mineral which can be bonded into an almost neutral refractory by firing at 1600°. The brick shows a high resistance to all forms of molten slag, and is stable in structure up to 1700°. Above this level the zircon dissociates into silica and zirconia. Zircon facings can be fixed to other types of refractory, thus avoiding some of the high cost.[6] Zirconia shapes, made up from ZrO_2, with the crystalline forms stabilised by lime, can be used up to 2200°. They are much too expensive for normal work, but where high electrical resistance at temperatures above 1500° is required the cost may be justified.[7]

SOAPSTONE

The naturally occurring acid magnesium silicate can be cut into blocks, or ground and made up into brick with a clay–iron bond. Resistance to molten alkaline slags is good, the furnaces for black liquor ignition (paper-making) being generally lined with soapstone brick. Of late, chromite brick has to some extent replaced a natural refractory which may be growing scarce.

NEUTRAL REFRACTORIES

These are used as an insulating course between the silicic fireclays or silica brick, which need only withstand heat, and a basic refractory which has to resist the action of molten metal or alkaline slags. Basic refractories are less reliable than fireclay and a good deal more expensive. The joint between the two types of brick is clearly a weak point, and must be made by two or three courses of neutral brick. In normal furnace practice this neutral brick is made up from chromite, a natural iron-chrome ore of approximate composition $FeCr_2O_4$. The ore is bonded with a little fireclay or magnesium silicate to give a finished brick of high thermal conductivity and reasonable refractoriness (Figs. XVI–1 and 9). The refractoriness can be increased by incorporating magnesite, but naturally this destroys the neutral character to some extent. The bricks tend to be fragile, and are sometimes made up with a thin iron casing. The cost is not greatly increased, and the bricks are easy to lay, with the casing melting and oxidising in use to a firm bond between the bricks proper.

Two alternatives to chromite brick are available in non-oxidising conditions. These are silicon carbide (carborundum) and carbon shapes, both excellent refractories with a safe working temperature at least as high as any silica or fireclay complex. The failure of either is commonly due to the bonding agent employed. Carborundum particles are best bonded with glue and fired cautiously to 1700° C., when the carbide itself sinters and takes over from the glue residues, crystallising in a form which is stable up to 2000°. A well-made brick will only expand by 0·5% from 0° to 1000°, while the thermal conductivity falls from 100 to 58 over the same temperature range. This high conductivity is accompanied by much higher emissivity[8] than that of ordinary firebricks, making it possible to replace directly heated reverbatory furnaces by muffle forms in many metallurgical operations. Silicon carbide has no catalytic action in the decomposition of gaseous carbon compounds at high temperatures, and is therefore particularly suited to the operations of high-temperature cracking and "reforming" in the petroleum industry.[9] Resistance to liquid acids at lower temperatures is quite good, and the bricks have been used in oleum plants. This is unusual, as refractory silica bricks are disintegrated by hot sulphuric acid. Both carborundum and chromite are used as "ramming" mixtures, being spread over a furnace floor in paste form as asphalt is spread on a road. The binder is heavy coal tar, bitumen, or glue, and the furnace is fired cautiously until the mixture has dried out.

Carbon refractories are built up from finely ground coke or graphite, bonded by pitch or artificial resins. Suitable firing can produce graphitic blocks with very high thermal conductivities. Figures as high as 720 have been quoted, but these are normally for shapes designed to work at lower temperatures and resist acid liquors. The high-temperature refractory will have a lower conductivity, but it will certainly be higher than any other suitable material. The thermal expansion is only 0·65% between 0° and 1000°, and the carbon surface can be made quite hard enough to resist all normal erosion. Blast-furnaces have been lined with carbon shapes with great success, and the material is unreactive to anything except oxidising agents. The only obvious drawback is the low density, which calls for special locking forms to hold individual blocks in their place. As the latest development in neutral refractories, carbon shapes are still in an experimental stage, and may have a very substantial future.

BASIC REFRACTORIES

These are essentially sintered magnesium oxide, in the form of periclase, a crystalline and non-reactive form of MgO. The more basic oxides, such as lime, hydrate and disintegrate on cooling. The crude refractory earth for burning to grog usually contains some iron oxide, and this aids conversion to periclase, being itself converted to a stable "spinel" of the general form $MgFe_2O_4$. The well-fired grog is crushed and bonded with a little lightly fired magnesia, setting to a hydraulic cement with water, Firing gives finished bricks which will stand loads up to 1550°, failing by shear rather than by thermal softening (Fig. XVI–10). The properly fired brick should consist almost entirely of periclase or a steady shrinkage occurs in use. Thermal conductivity figures can vary widely with porosity, as shown in Fig. XVI–11, but decrease fairly sharply with temperature. Even with this drawback, conductivity is normally higher than with acid bricks.

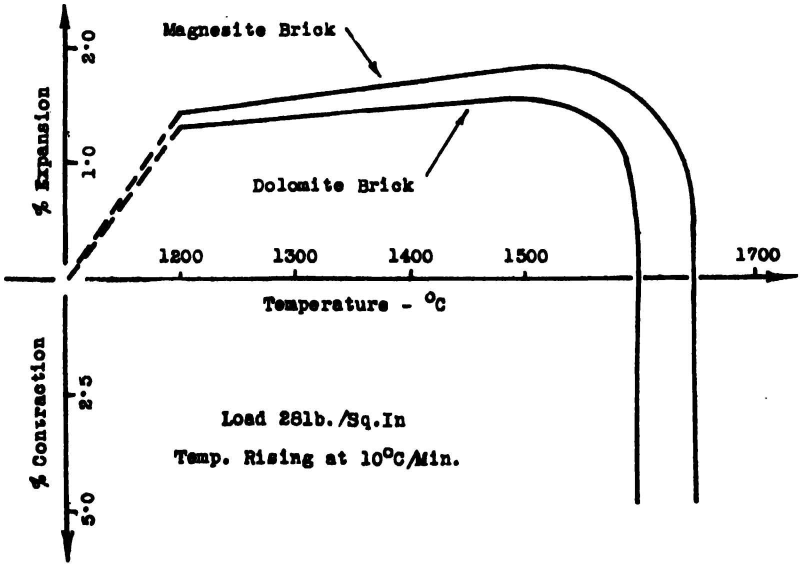


FIG. XVI–10.—REFRACTORINESS UNDER LOAD (ALKALINE REFRACTORIES).
(Courtesy of General Refractories, Ltd.)

Magnesite brick is absolutely essential in the building of steel melting-furnaces, and is generally used wherever molten metals must be contained. The bricks are subject to spalling and cannot be used in the lining of metal ladles, where sudden temperature changes occur. It is possible to correct this spalling tendency to some extent by careful grog sizing and bonding, but a magnesite–chrome complex brick has been developed which is essentially resistant to thermal shock, while at the same time it is basic enough (70–80% MgO) to resist the metal. Molten alkalies, as met with in caustic soda recovery, have no chemical action on the magnesia brick, but the surface is not very resistant to erosion, and again the harder chrom-magnesite can be used with advantage. It will be appreciated, from Fig. XVI–1, that the refractoriness is not diminished by substituting the chromium-bearing mixture. Lime and cement kilns have been lined with magnesite bricks, but they are rather fragile for such work, and are only used when the presence of molten metal more or less demands it. Magnesite in dead-burned form is used as a ramming powder, with pitch as a binder, but gives a rather porous structure on firing. Metal-cased bricks, with the thin iron shells mentioned above, can be used to overcome initial fragility, but the final structure is still friable.

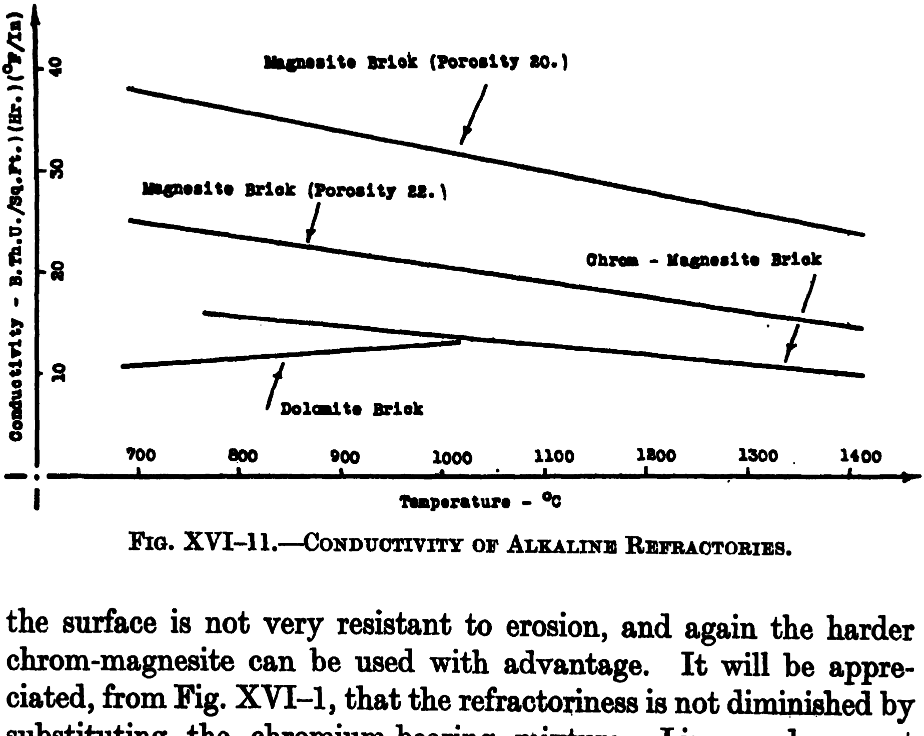


FIG. XVI–11.—CONDUCTIVITY OF ALKALINE REFRACTORIES.

Mixtures of magnesia with chromium oxide have been used for brick-making with a wide range of composition, from 80% down to

30% of MgO. Chemical properties follow the magnesia content until an almost neutral brick is obtained. A magnesium silicate complex, "forsterite", with the approximate composition $2MgO.SiO_2$, has a refractoriness almost as high as chrom-magnesite, with reasonable resistance to both metals and slags. It has been used for furnace roofs, so that it would appear less susceptible to spalling than the pure magnesite.

Dolomite bricks, from mixed carbonates of calcium and magnesium, must be stabilised by the addition of clay or magnesium silicate if the lime formed in burning is not to rehydrate and break up the brick. A stabilised dolomite brick can be regarded as a somewhat inferior magnesite shape, with the same tendency to spall, but with lower conductivity and refractoriness. The main attraction, of course, lies in cheapness via-à-vis the magnesite mixture.

FURNACE BUILDING AND MAINTENANCE

Whatever the form of firebrick used, it must be laid with considerable care, using the thinnest possible joints. These, as with acid-resisting brick, form the weak points of a furnace wall, even though the mortar is chosen to match the brick as closely as possible. Bonding of the bricks follows normal building technique to a large extent, though a greater use is made of special shapes. Even with the greatest care in construction, all refractories deteriorate in service, and a life of about five years is the most that can be expected if high efficiency is required (as low as six months in very severe conditions). Walls of furnaces may be cooled and patched, but often the cooling does more damage than the patching has repaired. Where brickwork must be appreciably gastight, as in coal carbonisation, hot patching has been recommended.[10] The hot brick is sprayed with a cement slurry, and all small cracks will be filled, though some spalling will inevitably ensue. The process can easily be used in a maintenance cycle, and can be supplemented by other means for stopping up large holes. These include plugging with cement putty, or building up the sides of the hole with a jet of molten refractory from an oxy-coalgas spray gun. When labour and materials are readily available, a cycle of pulling down and rebuilding at regular intervals is probably the best method of maintenance. For full details of furnace design, the reader should consult one of the special treatises on this subject, such as that by Trinks.[20]

REFRACTORY INSULATING BRICK

Heat must obviously be conserved in furnace work, except in the rare cases in which a "cold face" on the outside of a refractory wall is required to support the partly melted brick within. The primary function of a good refractory is to support the furnace load without distortion or collapse. Only in a secondary degree is it an insulator of heat, and this insulation must be supplied by special brick forms. Ordinary firebrick has a porosity of from 15% to 25%, and conductivity is closely linked with this. By increasing porosities to 50–60%, it is possible to reduce the conductivity to one-tenth of its previous value, as shown in Fig. XVI–12. Unfortunately this change is accompanied by a marked drop in refractoriness, and fireclay insulating brick is very little use at temperatures in excess of 1000°. Bricks based on silica or alumina are available with a "ceiling" which may be as high as 1500°, but even these tend to lose their insulating qualities gradually in service. This is due to the partial collapse of pore structure within the brick, accompanied by shrinkage and cracking.

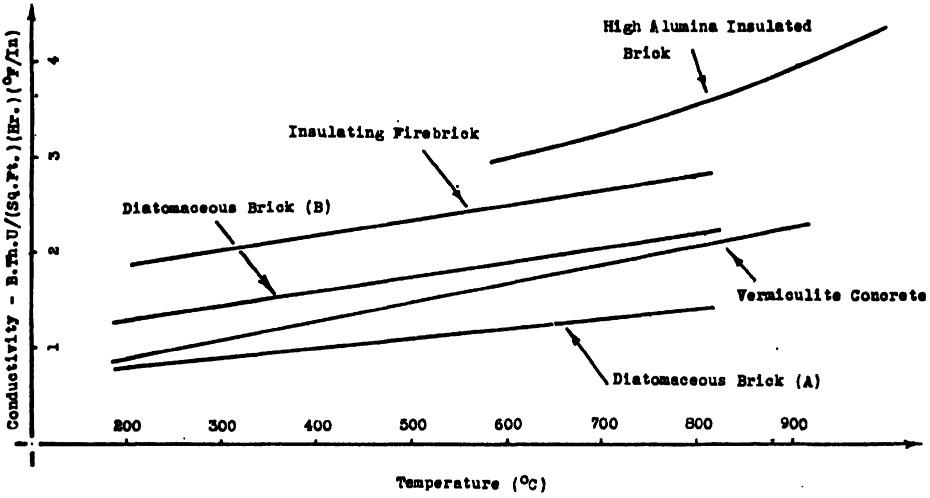


FIG. XVI–12.—CONDUCTIVITY OF INSULATING MATERIALS (High Temperatures).

These expanded shapes are made by incorporating into the raw mix a proportion of cork dust, coal, or gas-producing mixture, together with a bond which holds the brick together after light firing. By the use of an aggregate having already a micropore structure, as in diatomite or exfoliated vermiculite, it is possible to increase porosity still further. These two are natural products, not readily available and rather costly, but appear to give the most efficient insulation at temperatures above 600°. Diatomite is almost pure silica, laid down in various complicated micro-structures by prehistoric living organisms.[11] It will presumably suffer in the same way as silica brick from form changes, and is not recommended for use above about 1100°. Vermiculites are complex silicates containing iron, aluminium, and magnesium,[12] and can hardly be suitable for any higher temperatures. It is possible, by sintering together hollow spheres of fused alumina, to obtain a brick which will stand temperatures as high as 1500°, but the thermal conductivity is rather high (Fig. XVI–12).

INSULATING CONCRETES

These are very simply made from crushed insulating brick and alumina cement, reflecting in their properties the aggregate from which they have been made. Thus a vermiculite concrete containing about 4 parts of aggregate to 1 part of cement will only weigh 30–40 lb./cu. ft., can be cut with wood-saws, and will stand up to temperatures in the region of 1000°.[13] The proportion of water to be used does not appear so critical as with ordinary concrete for structural purposes. Preformed blocks, perhaps incorporating some fireclay grog, can be built into light-weight furnaces, and are easily cut into special shapes. In general, such concrete blocks are not so thermally resistant as the properly fired brick of the same approximate composition.

PACKED SOLIDS

Diatomite and vermiculite can be packed tightly into any formed space, giving a cheap construction which is almost as good as a proper insulating brick. The resistance to temperature is no better, and some shrinkage sets in around 800°. Silica aerogel, a pure form of silica with a packing density of less than 5 lb./cu. ft., will give layers with a conductivity as low as 0·20, but shrinkage and failure can start at about 600°. In any case the aero gel is expensive, and only suitable for very special work. Silica fibre mats are now available in bulk, while similar mats of glass or slag fibre have long been available. These three fibres have very similar conductivities (Fig. XVI–13) and packing densities varying from 10 to 20 lb./cu. ft. Glass and slag fibres collapse rapidly at any temperatures above

500°,[14] but silica can be used up to 1100°, when the conductivity of a typical packing has risen to about 2. By a careful choice of raw material it is possible to obtain slag fibres which are stable up to 775°.[15] All these fibrous insulators can be woven into blankets and combined with thin metal foils to give special covers. It is probable that all such fibrous forms are inherently unstable, and therefore they tend to age in service, probably by slow crystallisation and crumbling.[16]

GENERAL INSULATING MATERIALS

This would appear to be an appropriate place to deal with the multitude of insulating materials which have been used in chemical plant. They range from natural products such as cork and wood through asbestos, magnesia, and expanded rubber to foamed organic polymers. Probably the most widely used "lagging" is a plaster of light magnesium carbonate and asbestos fibre. A mixture of 85% $MgCO_3$ and 15% asbestos fibre has a conductivity of about 0·4–0·5, as shown in Fig. XVI–13. Asbestos fibre alone has almost the same conductivity, but is not so easy to apply and more expensive. The

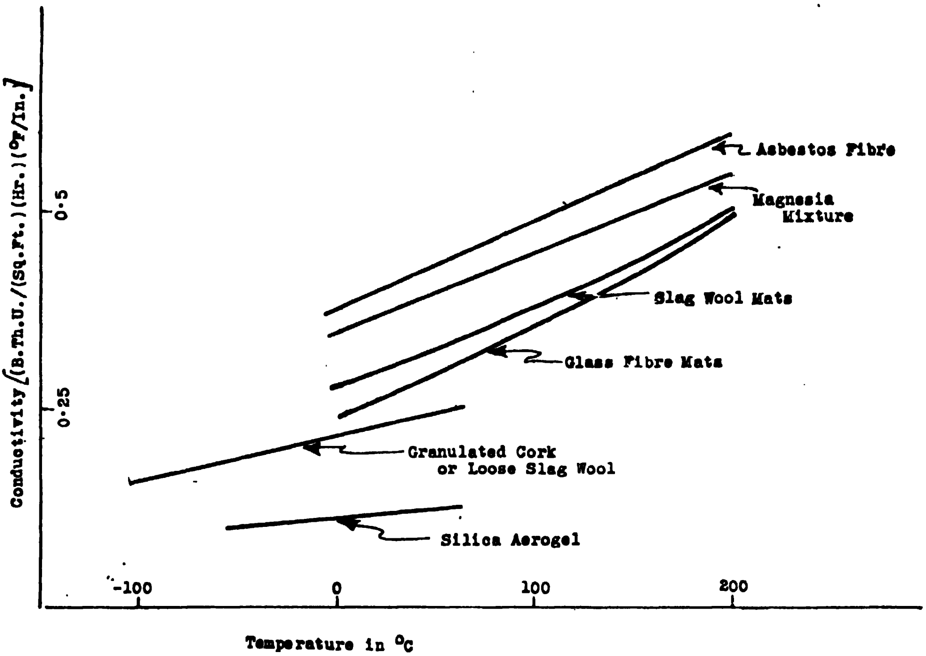


FIG. XVI–13.—CONDUCTIVITY OF INSULATING MATERIALS (Low Temperatures).

mixture is quite suitable for all temperatures up to 300°, and certain forms of asbestos can be used at 400°. A mixture of diatomite and clay is often used as an inner layer on hot surfaces before applying the more efficient magnesia mixture. Whatever the composition of the porous mass, overall conductivities cannot fall below that of the enclosed air —0·18 at ordinary temperatures.

In work at temperatures below atmospheric levels, it is just as important to insulate as in plant where heat must be conserved. This insulation must keep heat out, and operation is complicated by the condensation of water from moist surrounding air. Although the condensate turns to ice in many cases, it still remains a good heat-transfer medium, and insulating material must be protected from waterlogging. Ordinary coverings are difficult to isolate, and the pores are soon filled with a solid ice mass. This can be overcome if the air sacs are completely enclosed—no intercommunicating channels. Certain forms of foamed glass have been devised for which this property is claimed. They have densities of the order of 10 lb./cu. ft., and can be cut with ordinary saws.[17] The conductivity is about the same as a magnesia mixture. Most of the synthetic polymers of commerce can be obtained in frothed forms, and may be even less permeable to water vapour than the frothed glass. Blocks of these solid foams would form a very good "lagging", but the joints must be carefully sealed against the entrance of moist air. Ice forming at these points could force the insulating layer away from the plant wall. It is quite a common practice to make no attempt at careful proofing, but to use a loose fill of, e.g., slag wool, crumpled aluminium foil, or glass fibre in a metal jacket, and to connect this space to the atmosphere through a number of breathing ports provided with dehydrating agents. Silica aerogel suffers from the fact that it is a potent absorbent for water vapour, but it can be used as a filler for vacuum jackets, giving conductivities as low as 0·01.[18]

The optimum thickness of insulating material for any plant section is determined by balancing the cost of the lagging against the cost of heat (or units of refrigeration) saved. A number of general formulae have been suggested,[19] but these are usually for a specific case, such as the requirement for a pipe-line or a cylindrical vessel. It is better to treat each case on its merits, remembering to take into account such factors as the nuisance of moisture condensation on cold pipes, or the accident potentiality of hot exposed surfaces.

REFERENCES

1. B.S. 1902 (1952).
2. Barrett, L. R., "Materials of Construction", p. 246.
3. Hussey, A. V., *Chem. and Ind.*, 1937, **53**.
4. Partridge, J. H., *J. Roy. Soc. Arts*, 1939, **87**, 4495 (p. 227).
5. Barrett, L. R., "Materials of Construction", p. 243.
6. See, e.g., B.P. 581598.
7. Baldwin, W. J., *Chem. Engng. Progr.*, 1948, **44**, 875.
8. Geiger, C. F., *et al.*, *ibid.*, 1948, **44**, 933.
9. Turner, A. A., *et al.*, *ibid.*, 1952, **48**, 281.
10. Myhill, A. R., *Gas Times*, 1952, **70**, 51.
11. Salmon, F. G., *Proc. Chem. Eng. Grp.*, 1938, **20**, 20.
12. "Mineralogy", Dana, E. S., John Wiley, 4th edition, 1949, p. 674.
13. Jones, N. C., "Materials of Construction", p. 55.
14. Parker, L., and Foster, J. L., *Chem. Engng. Progr.*, 1947, **44**, 937.
15. *Industrial Chemist*, 1952, **28**, 407.
16. Butterworth, A. V., *Chem. Engng. Progr.*, 1947, **43**, 597.
17. Sanders, U., *ibid.*, 1951, **47**, 804.
18. White, J. F., *ibid.*, 1948, **44**, 647.
19. See, e.g., B.S. 1334 (1947), or Lyle, O., "Efficient use of Steam", Chapter 4, H.M.S.O., 1947.
20. Trinks, W., "Industrial Furnaces", John Wiley, 3rd edition, 1951.

CHAPTER XVII

VITREOUS SILICA AND HARD GLASS

THESE two materials are classed together as representing almost the final resort in corrosion resistance to hot acids and in addition a very high degree of passivity to sensitive chemicals. In physical structure both are "glasses" or supercooled liquids, and both tend to become "devitrified" to a crystalline form, with mechanical breakdown. A more present weakness, however, is that neither has much resistance to mechanical shock. This is particularly the case with silica, whether in the more usual translucent "Vitreosil"[1] or in the clear transparent form. The hard glass used in chemical plant, and normally marketed under the names "Pyrex"[1] or "Hysil",[1] is less susceptible to accidental breakage, but its life is usually terminated by some catastrophe.

VITREOUS SILICA

This is almost pure silica, made by fusing a suitable sand in an electric furnace. The melt for Vitreosil is never quite fluid, and the finished product contains numbers of fine bubbles, conferring a translucent appearance. The porous structure is also somewhat permeable to gas, especially at high temperatures or at very low pressures. It is practically impossible to maintain a high vacuum inside a Vitreosil tube. The maximum weight of a single batch for melting is about 500 lb., and this puts a limit to the size of a single piece of equipment. The largest container that can be made at present is of the order of 20 cu. ft. capacity, and pipe sections are limited to 30 in. bore (and 4 ft. in length). Manufacture to narrow engineering tolerances is difficult, and a 30-in. bore pipe may vary in diameter by as much as ½ in. As a result, joints between pipe lengths are normally made by spigot and faucet methods with a soft packing. Individual pipe ends may be belled out slightly and ground to take a flange fitting, but this is not standard practice. Again, long coils of pipe may be built up *in situ* from smaller lengths, using an oxygen-hydrogen blowpipe, but the technique is difficult to acquire. Finished work of this form has the advantage that no annealing is required, though it is generally recommended to remove minor stresses which may contribute to a later breakage. Tubing can be cut by ordinary carborundum wheels, using water-cooling, but special wheels are available. Holes can be drilled by metal tubes, fed with an abrasive powder, as in the well-known techniques for drilling glass plates.

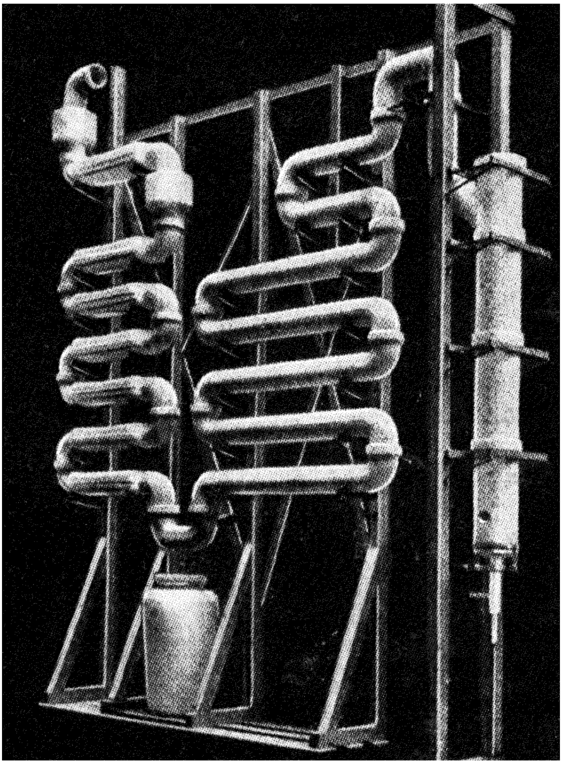


Fig. XVII-1.—Hydrochloric Acid from H_2 and Cl_2 Plant in Vitreosil. *(Courtesy of The Thermal Syndicate.)*

The ultimate tensile strength is set rather vaguely at 10,000 lb./sq. in. As with all brittle solids, this strength is largely determined by minute surface flaws, which can set up local stress concentrations, and if these are almost eliminated by drawing out the silica into long thin threads the tensile strength is greatly increased. Such effects are not of interest in chemical plant work, where a large silica section should not be put under any stress greater than 100 lb./sq. in. Compressive strength can be very high, but is seldom utilised, except in the specialised clear silica ports for experimental high-pressure work.

Vitreous silica is extremely resistant to thermal shock, with a coefficient of thermal expansion as low as 5×10^{-7}, only one-fifth that of hard glass. The thermal conductivity is low at 9·5 B.Th.U./(sq. ft.)(hr.)(° F./in.), but this represents a wall coefficient of 77 B.Th.U. for an ⅛-in. wall, and temperature differences can be very high without risk of breakage. It is common practice to build heaters in which the metallic heating elements are pressed against the silica, the ordinary laboratory furnace being a case in point. Working temperatures should not exceed 800° if devitrification is to be avoided, but for short periods a temperature of 1000° does no great harm. The reaction between chlorine and hydrogen can be effected in an Vitreosil combustion chamber, with direct air-cooling of the outside wall. A gas with no impurities other than excess of the two reactants is obtained; if the combustion is followed by cooling and absorption in a silica train, as shown in Fig. XVII–1, the acid solution will be free from any metallic impurities. The extreme inertness of silica is shown also in the preparation of "conductivity" water by straight distillation (Fig. XVII–2). The Vitreosil parts of any large plant must be carefully supported on wood or steel framing, with the smallest possible stress on any pipe joint

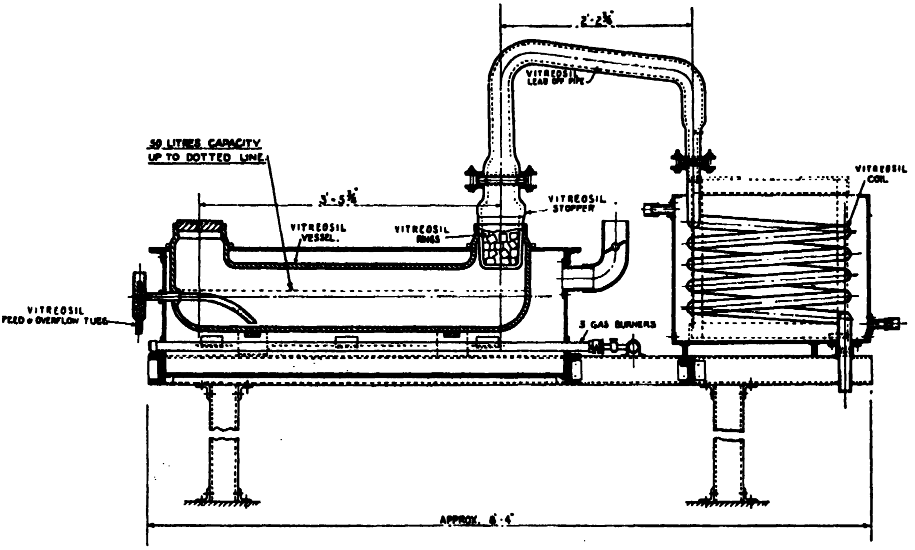

2'-2¾"
VITREOSIL LEAD OFF PIPE
50 LITRES CAPACITY UP TO DOTTED LINE
VITREOSIL COIL
3'-5¾"
VITREOSIL STOPPER
VITREOSIL VESSEL.
VITREOSIL RINGS
VITREOSIL FEED & OVERFLOW TUBE
3 GAS BURNERS
APPROX. 6'-4"

FIG. XVII–2.—VITREOSIL PLANT FOR PURE DISTILLED WATER.
(*Courtesy of The Thermal Syndicate.*)

(Fig. XVII–3). The outlet pipes from sulphuric acid concentrators must withstand gas temperatures of 1000°, with boiling acid at 300°, and lead direct to coolers where the water may be at 15°. The only materials which can stand up to such conditions of heat and corrosion are Vitreosil and perhaps high-silicon iron. Centre sections of the acid coolers following this outlet are also in Vitreosil, while coils of 3-in. bore and 120 ft. long can complete the cooling. Resistance to attack by sulphuric, nitric and hydrochloric acid is absolute, and the only fault is excessive fragility. It is a disadvantage in the operation of Vitreosil plant that it is opaque, with a rough outer surface that soon grows dirty and undistinguishable from metal. Glass is recognised at once and gets gentle treatment, but the less conspicuous silica is handled more roughly.

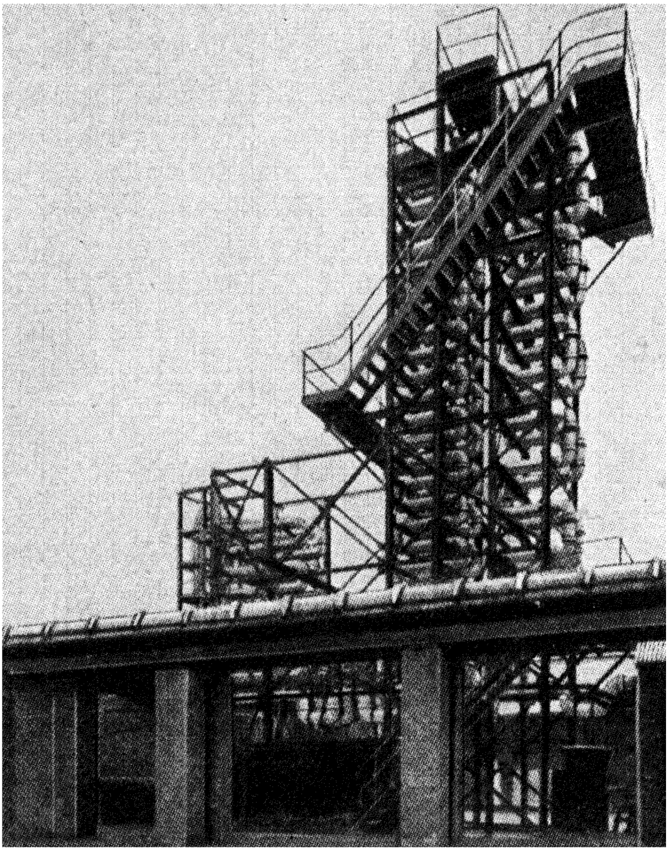


Fig. XVII–3.—Large Vitreosil Condensers and Gas Scrubbers

(*Courtesy of The Thermal Syndicate.*)

The spigot and faucet joints in a pipe-line are particularly susceptible to breakage, and the packing should always be a soft putty. Some of these have already been mentioned in the appropriate chapter (XIV), but one which has been specifically recommended for Vitreosil has the composition

Asbestos Fibre	44 parts	Whiting	20 parts
Tallow	4–5 parts	Boiled Linseed Oil	23 parts

This is used as a backing to asbestos rope, and fitters are warned to use great care in assembly. A joint of this kind will have little strength to withstand gas pressures, and it may be reinforced with a thin layer of hardening cement made from sodium silicate and asbestos in the usual way. Proprietary cements are available which give better joints capable of resisting high temperatures, but they are still brittle.

Transparent silica—clear fused vitreous silica—is just as fragile as Vitreosil and much more costly. It is only used for special purposes where light or energy transmission is required. A window of clear silica is almost completely transparent, passing 93% of the visible light through 1 metre of thickness, compared with 63% for good optical glass. Transmission in the infra-red, where most heat is radiated, is also very good, and this particular property has been made the basis of evaporator designs for heat-sensitive substances.[2] Even in the transparent form the silica is still somewhat permeable to gases.[3]

A form of silica glass has been made by fusing a complex sodium silico-borate mixture and moulding to shape.[7] The shape is heated for some hours at about 600°, when the structure of the solid is resolved into two phases, one of nearly pure silica and the other of acid-soluble sodium borate. This latter can be leached away to give a skeleton vessel of porous silica. Further heating to 1000° will cause considerable shrinkage, but a vitreous silica shape is left, without the need for such high temperatures as are normally involved. The method does not appear to have found any extended application at present.

HARD GLASS

The softer soda glasses are never used in chemical plant work, as they are less mechanically reliable and more reactive than the higher-melting glass mixtures known for many years as "hard glass".

Mechanical reliability is bound up with low coefficients of thermal expansion, which reduce the amount of internal stress left in any plant section fabricated by fusion welding. This low thermal expansion is generally incompatible with a glass of low melting-point, owing to specific material properties. Alkali metals must be substituted by boron or aluminium in order to give a silicate with low thermal expansion, and the softening temperature of the resulting glass is thereby increased. It is still possible, however, to obtain a glass composition which enables easy working with an oxy-coalgas blowpipe and fabrication into a variety of complicated forms. The thermal expansion is low enough to give stable structures without the very careful annealing which a soft soda glass requires.

A wide range of glass compositions has been explored, and a certain amount of secrecy exists as to the precise composition of a particular type, but the two set out in Table XVII–1 can be taken as typical of a borosilicate and an aluminosilicate glass. Either can be used for chemical plant work, but the borosilicate is the more common.

TABLE XVII–1

Constituent	Type A	Type B
SiO_2	80·5	58·7
B_2O_3	12·9	3·0
Al_2O_3	2·2	22·5
CaO	—	5·9
MgO	—	8·4
Na_2O	3·8	1·1
K_2O	0·6	0·2

The coefficient of linear expansion between 15° and 350° is from ($30–33 \times 10^{-7}$), as compared with (5×10^{-7}) for silica and ($80–90 \times 10^{-7}$) for ordinary soft soda glass. Somewhat lower coefficients have been claimed for proprietary forms such as "Pyrex", and it is generally necessary to see that all of a plant is made up from one type of glass. The thermal conductivity is lower than that of vitreous silica at 7·8 B.Th.U., but the greater mechanical reliability allows of a thinner wall, such as 0·06 in. for a 2-in. bore tube. A wall coefficient of 130 B.Th.U./(sq. ft.)(hr.)(° F.) is thus obtained, which is of the same order as that of a liquid film, and overall coefficients of the order of 100 B.Th.U. have been obtained in Pyrex glass equipment. The ultimate tensile strength of hard glass will again vary with degree of working, but the more easily melted glass is relatively free of surface flaws, and safe load figures of the order of 2000 lb./sq. in. are accepted. The 2-in. pipe with a 0·06-in. wall will thus have a working pressure of 120 lb./sq. in.

The main risk, as with silica, is of accidental breakage, but perhaps the chance is smaller with a material which is stronger and more easily recognised. Obviously glass plant should be carefully supported, as shown in Fig. XVII–4. The evaporative cooler of the figure is made up from 480 lengths of 2-in. bore pipes, each 10 ft. long, with standard flange joints and return bends. This piece of plant was built for cooling concentrated hydrochloric acid, and contained some 2500 sq. ft. of corrosion-proof cooling surface. Coupled with a stoneware pump and a stoneware absorption tower, this cooler would represent perhaps the best form of HCl absorption unit for normal use. The flanged joints of these pipes are quite usual for glass plant, and can be made in much larger sizes, shown in

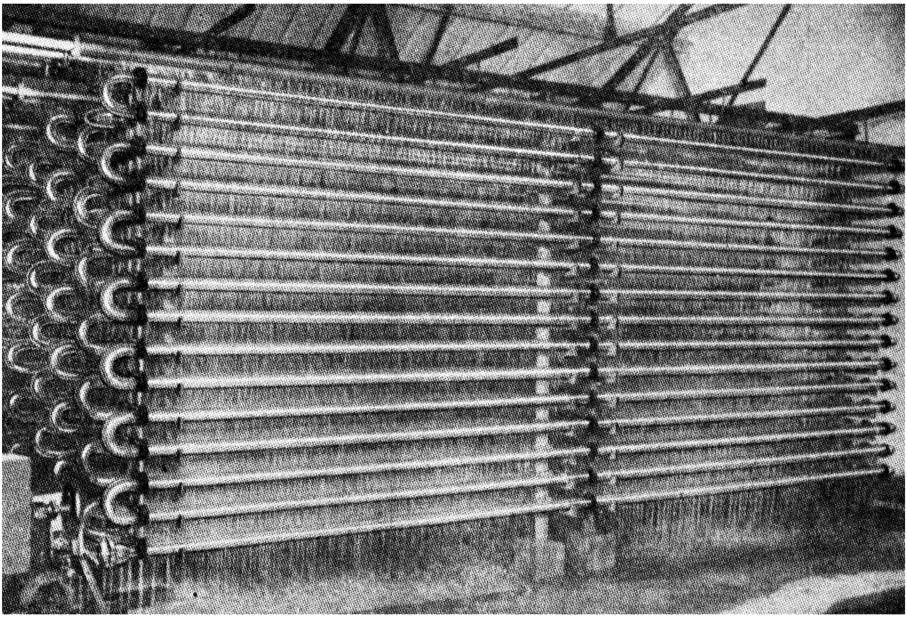
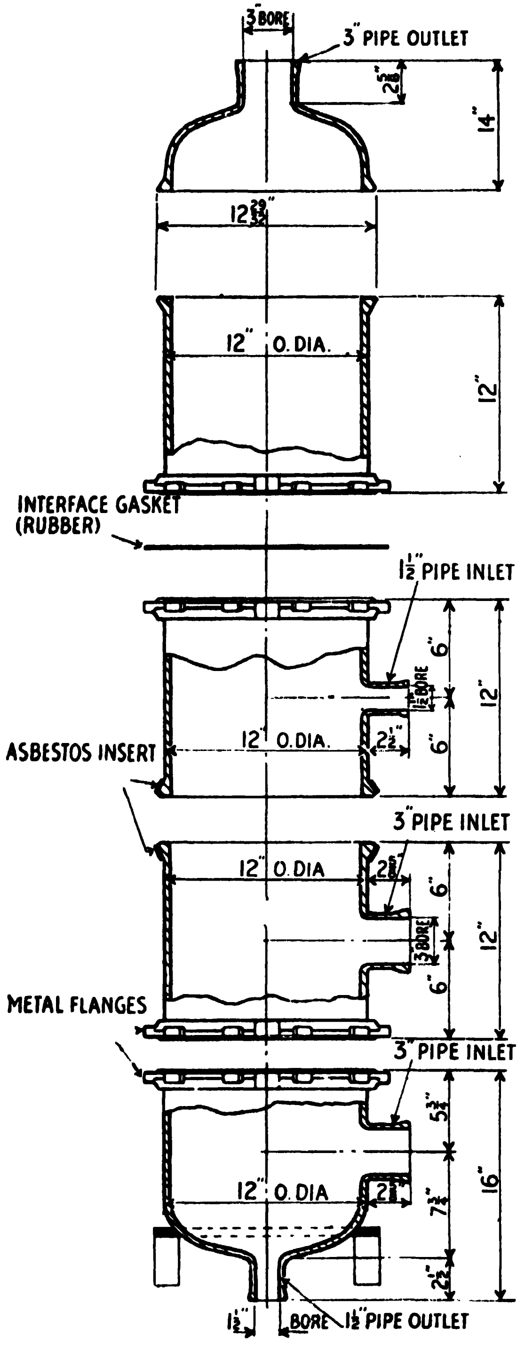


FIG. XVII–4.—SPRAY COOLERS IN GLASS PIPE.
4,800 ft. of 2-in. Bore Pipe.
(Courtesy of J. A. Jobling & Co.)

Fig. XVII–5. A flange can be up to 12 in. diameter, and with their aid such complicated pieces of apparatus as the scrubbing tower shown in Fig. XVII–6 can be built up. These plants are designed for complete corrosion resistance, and obviously the joint between the flanges represents a point of possible weakness. Gasket rings have been made from asbestos, rubber, or oil-resistant synthetic rubber. More recently polythene and teflon (Chapter XIX) have been introduced; the latter, when available at a more reasonable price, will probably make an ideal all-purpose gasket.


3" BORE
3" PIPE OUTLET
2⅝"
14"
12 29/32"
12" O. DIA.
12"
INTERFACE GASKET (RUBBER)
1½" PIPE INLET
6"
1½" BORE
12"
12" O. DIA.
2¼"
6"
ASBESTOS INSERT
3" PIPE INLET
12" O DIA
2⅝"
6"
3" BORE
12"
6"
METAL FLANGES
3" PIPE INLET
5¾"
16"
12" O DIA
2¼"
7¼"
2¼"
1½"
BORE
1½" PIPE OUTLET

ALL DIMENSIONS ARE APPROXIMATE

Fig. XVII–5.—Glass Absorption Tower. (*Courtesy of J. A. Jobling & Co.*)

Of course, it is possible to dispense with flanges and gaskets altogether, and to fuse the whole plant together by the normal methods of glass-blowing. This is not really difficult for skilled operators, and the main problem is the increased fragility. Such construction has the advantage of being perfectly vacuum-tight, and can be used for all high-vacuum work, or for a process in which air inleakage would be extremely undesirable. Very large plants were built in this way during the early stages of atomic energy development.[4] Flanged joints do give a greater flexibility, and allow the plant to be taken down for cleaning. In many all-glass plants it is necessary to ensure bacterial sterility, and this can easily be obtained by flushing out with

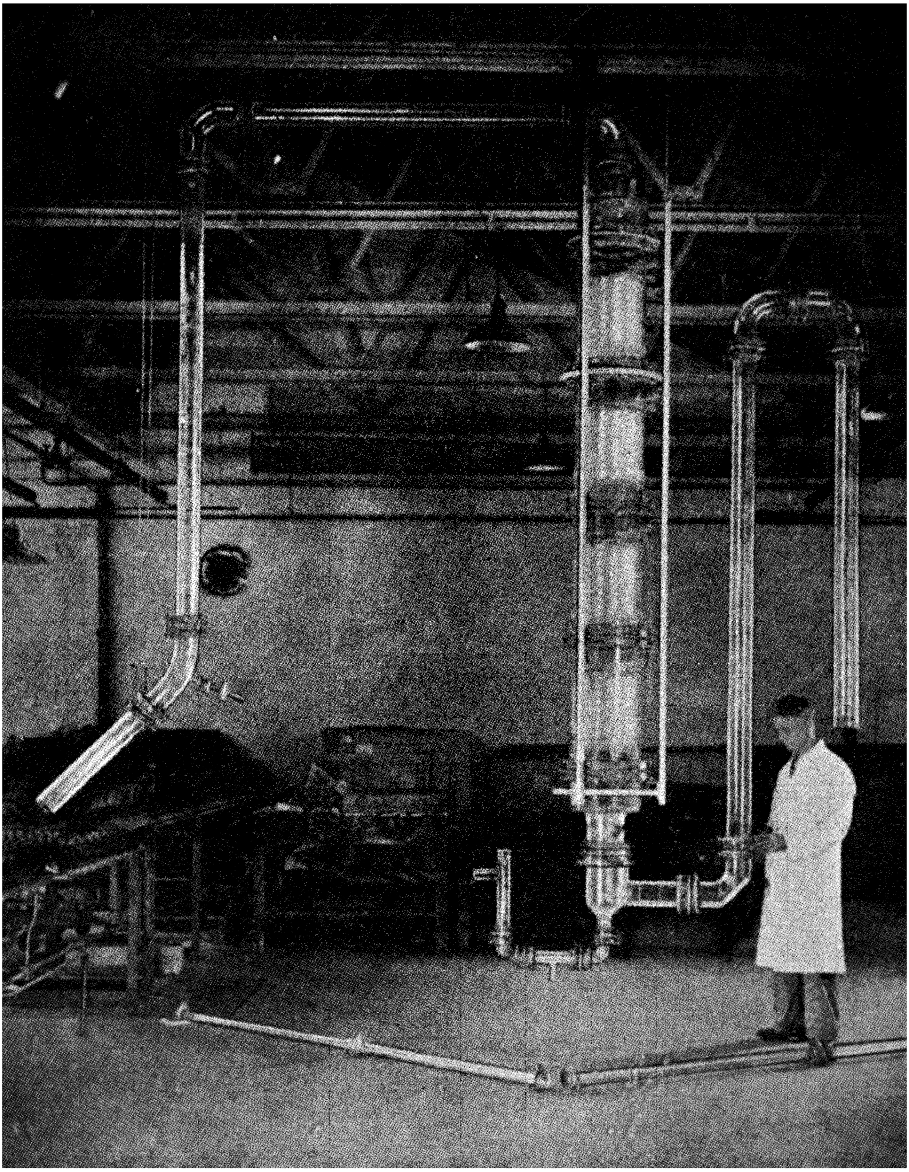


FIG. XVII–6.—GLASS SCRUBBING TOWER WITH INTERNAL COOLING.
(*Courtesy of Quickfit & Quartz, Ltd.*)

detergent solutions followed by a disinfectant. The smooth hard surface offers no lodgement for bacterial colonies. The filter shown in Fig. XVII–7 is designed to this end.

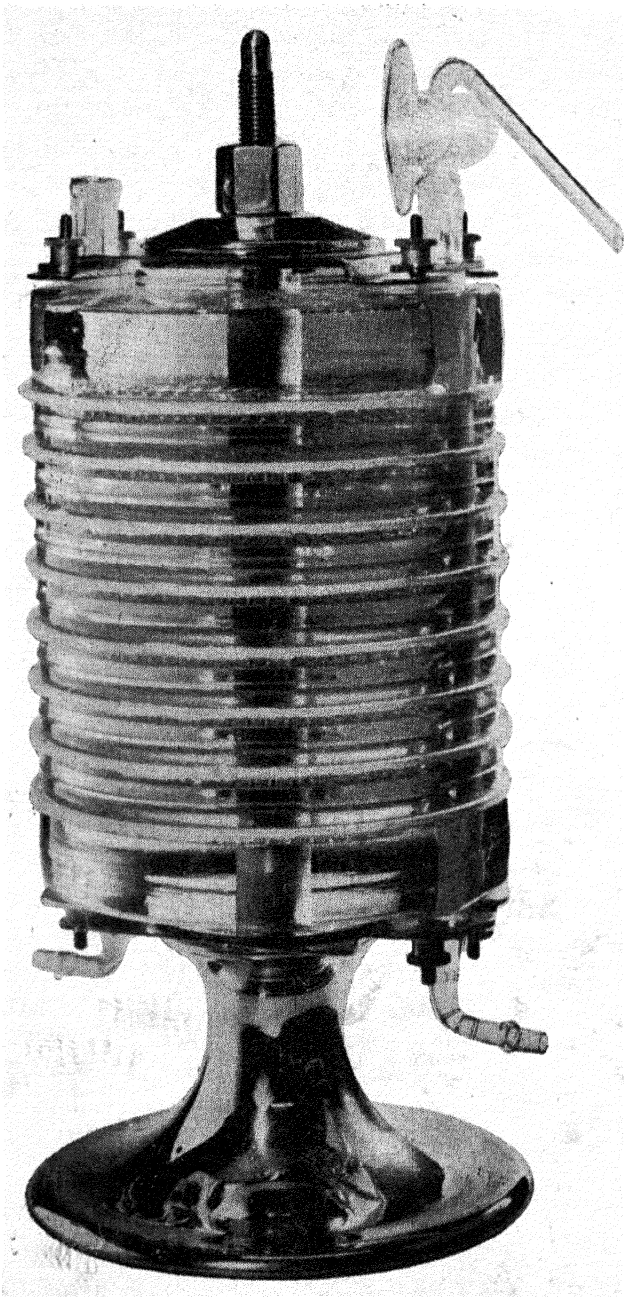


FIG. XVII–7.—ALL-GLASS FILTER PRESS.

(*Courtesy of British Filters Ltd.*)

The thermal resistance of hard glass is quite satisfactory up to 300° and reasonable up to 400°, but this is definitely the working limit. It is no longer possible, as with silica, to arrange for very high temperature differences across a glass wall and a maximum of about 150° has been suggested. This represents the limit for thermal shock, such as might be caused by turning steam into a cold pipe. The working limits of alumina-glass mixtures are wider,[5] but these are not so easily worked by hot moulding and gas fusion as the borosilicates. It might be possible to combine the two through a judicious use of flanged joints, but no such plant is on the market, as far as is known.

Transmission of light through a borosilicate glass is much worse than through silica, especially outside the visible spectrum. Again the alumina glasses are better, and in fact a special mixture containing calcium, magnesium, and aluminium (no silica) is better than fused silica for transmission in the infra-red. Although hard glass is almost impermeable to gases, it is still not quite so good as common soda glass, and the permeability must be taken into account in very high-vacuum work.[6]

CHEMICAL RESISTANCE

This is almost complete for both Vitreosil and hard glass with all acids except hydrofluoric and perhaps hot concentrated phosphoric acid. The former gives a volatile fluoride with all silica-bearing glass, while the latter appears to break up the vitreous structure. Dilute alkaline solutions, containing up to 5% of free caustic soda, will have no particular action, although of course they are not normally handled in such expensive plant. Strong hot alkalies will attack either vitreous silica or hard glass. Pure water leaches out traces of metallic compounds from a borosilicate glass, but the rate of attack is so small that there is little or no action on the most sensitive chemicals. Silica is still more inert, as shown by its use in the manufacture of conductivity water. Neutral salts, in solution, will have no action unless the temperature is raised to a point at which reaction of the solid with the container can occur. This is unlikely with any solutions, except of course by accident.

COST

It may be assumed as a first approximation that Vitreosil costs about 30 pence and borosilicate glass 40 pence per pound, as simple

CHAPTER XVIII

WOOD

As in other fields of industry, the use of wood is steadily declining, but it is remarkable how slow this change may be in such fields as the manufacture of fine colours or the maturing of alcoholic liquors. Thirty years ago the framework of acid plant was almost always built up from heavy pine timber, but this particular construction has quite disappeared. The softness and resilience of a wooden frame, with its ease of construction and alteration, still appeals when plant in silica, stoneware, or glass has to be supported, but it is a little doubtful if any large plant, erected *de novo*, would be designed for wooden supports. Steel and wood are still combined in the support of lead work, but the main members are of steel. The principal uses of wood, therefore, are in the manufacture of tanks (vats) and filtering devices, with a very large specialised application in the packing of water-cooling towers. Wooden pipes are still made up for fume ducts, and sometimes for liquids, but represent historic survivals rather than modern development.

As a simple engineering material wood has a very high strength *along the grain*. Normal values range from 7500 to 10,000 lb./sq. in., and this for a material weighing less than a tenth as much as mild steel. It is possible to find special woods that are twice as strong as ordinary mild steel on a weight-for-weight basis. Unfortunately this is for ultimate tensile strength along the grain, and figures for strength across the fibres are very much lower. It is not possible to put ordinary timber under any cross-grain stress with safety, and only a plywood structure can be relied on for equal resistance in all directions. The cost of good-quality "softwood" is normally somewhat less than steel on a weight basis, but the supply position has fluctuated wildly over the last few years.

Wood has no fixed dimensions, and a single plank may vary in length with humidity changes by as much as $\frac{1}{8}$ in. to the foot. It can warp, twist, and split by internal stress in a quite arbitrary manner, and there is no real standard strength figure, since each tree is an individual. No two planks from a tree can be absolutely identical, and a great deal depends on the way in which the trunk of wood has been cut. The grain boundaries formed by the annual growth rings are presented at right angles to the surface in a "rift-sawn" plank (Fig. XVIII–1) but at very much smaller angles when "flat-sawn". The best wood comes from a layer midway between centre and outer sapwood, as the latter is soft and the heart wood is often slightly decayed. A straight grain, free from knots, is very desirable. Distorted grain means that the wood cannot easily be worked to a smooth finish and joints are poor, while long planks are more likely to warp if the grain is twisted. Liquids can seep through a wooden diaphragm much more readily if grain boundary paths are available, and a flat-sawn plank will present a much more effective barrier than one which is rift-sawn. It is clear, then, that all wood properties can only be taken as average values, and wide local divergencies can be expected. A few typical wood properties are shown in Table XVIII–1.

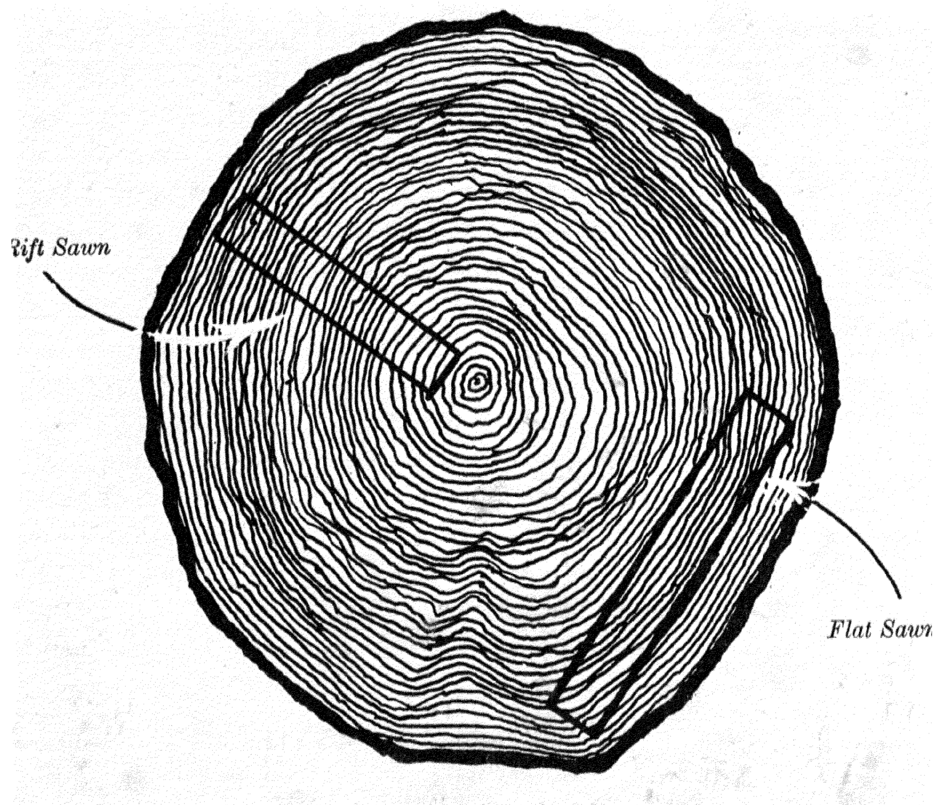


Fig. XVIII–1.

TABLE XVIII–1

Wood	Pitch-Pine	Spruce	Cypress	Douglas Fir	Redwood	Maple	White Oak	Teak	Lignum-Vitae
Density in lb./cu. ft.	28	26	32	34	28	44	47	41	72
Tensile Strength, lb./sq. in. —**along grain**	6300	6700	7200	8100	6900	9500	7900	8300	9000
Compressive Strength, lb./sq. in.	4000	4800	4700	6400	4500	5400	4400	6700	5300
Thermal Conductivity, B.Th.U./(sq. ft.)(hr.)(° F./in.)	—	—	0·83	0·77	0·76	1·16	1·22	—	—

It will be appreciated that this list comprises about 1% of the known varieties of wood. B.S. 589 and 881 name some 570 types of timber, with their place of origin, but do not pretend to be comprehensive.

According to generally accepted theories,[1] the chemical resistance of wood is bound up in a high content of α cellulose and lignins, with a low content of hemicellulose. A structure with a minimum of voids suggests low permeability and a small reaction area, but certain timbers have exceptionally well-sealed pores and this is an important factor in checking seepage of liquid contents. In a certain notable case, balsa-wood logs retained their original buoyancy after three months' immersion in sea water.[2] The chemical composition defined as desirable is found most fully in coniferous "softwoods" such as pitch-pine or Douglas fir. Cypress, redwood, Kauri pine and Caribbean pine are almost as good, and all these are light (28–34 lb./cu. ft.), straight-grained, and available in sections up to 20 ft. in length. Hardwoods, as used in furniture, are much more reactive, and when relatively unattacked often give coloured extracts. Burma teak, normally reckoned as a hardwood, is an exception to the general rule in that it is rich in α cellulose and still retains the relative impermeability which characterises hardwoods. This particular wood is familiar to most chemists as a material for laboratory bench tops, and when waxed and polished is remarkably resistant to all aqueous solutions. It is also resistant to insect life and not subject to wet or dry rot. Unfortunately supplies have long been inadequate, and there seems little prospect of any improvement in the position. White oak and maple, among the lighter of the hardwoods (44–57 lb./cu. ft.), owe their resistance more to texture than to composition, but have been widely used. A number of tropical woods, usually heavy and resembling teak, have been tried with indifferent success.[3]

Wood of all kinds is subject to attack by micro-organisms and insects, of which the former are much the more troublesome. Attack by the most usual organisms (*Merulius lacrymans* and *Poria vaporaria*) reaches a maximum when the atmosphere above the wood has a relative humidity between 85% and 90% and the temperature is between 25° and 30°. This corresponds with a minimum moisture content in the wood of about 22–24%.[4] A vat containing water will have the inner surface fully saturated, while the outer surface, if unpainted and exposed to the air, will be relatively dry. As a result the fungal attack cannot start except under surfaces which are protected from the air by sheathing with paint or laying flat on a floor. Painting of the outer wooden surface, by preventing drying, can bring about the very decay it was designed to prevent. As a consequence it is generally recommended that vats should not be painted, despite the somewhat unsightly appearance. However, when very corrosive solutions are being handled they may check the fungal attack, and painting with aluminium paint followed by corrosion-resistant varnish allows the outside of the vat to be hosed down freely after accidental spillage. The tendency of various woods to attack of this kind varies widely, and unfortunately is most marked with the chemically resistant softwoods, though Kauri pine is said to be extremely resistant.

The fabrication of wooden plant is an age-old craft, following the normal practice of carpentry, cabinet-making, and coopering. Table XVIII–1 shows the typical properties of wood used in vat construction. Such wood can be cut into long straight staves, with a section varying up to perhaps 12 in. by 3 in., and lengths up to 15 ft. The staves are planed and shaped to a good facing finish, and locked together with metal hoops, of strength sufficient to take the entire hydrostatic load. The expansion of wood when wet makes the joints perfectly watertight if properly made. Mild-steel hoops on a pitch-pine vat used for diazotisations in dilute HCl solution showed no signs of local corrosion after five years of almost continuous work. It has been suggested that the metal hoops be held away from the wood of the vat by small blocks of hardwood, rubber, or some such material, but this hardly seems necessary. Close contact between wood and steel can stimulate both metal corrosion and wood decay, and it might be better to specify plated hoops for long service. The art of vat-making has been established for hundreds of years; very large vessels have been noted historically and can be repeated today, as will be seen from Fig. XVIII–2. It is even possible to construct for steam-pressure resistance a vat of 7 ft. diameter, standing 45 lb./sq. in. gauge internal pressure.

Opinions differ on the ease of cleaning, and brewing practice is changing over to aluminium, stainless steel, or enamelled iron owing to the difficulty of keeping wooden surfaces in a sterile condition. On the other hand, makers of diazo colours experience no difficulty in cleaning vats between successive batches of different colour. When a cask has started to rot it is impossible to clean or use again for brewing and similar processes. Oak vats are particularly subject to this trouble, and in addition can cause corrosion by leached-out organic acids.[5]

Filter-press frames are often constructed in wood. The rectangular form and need for lightness in manual handling indicates special suitability where large frames are required. The limit of size for metal is generally set at 3 ft. by 3 ft., but wooden frames as large as 5 ft. by 4 ft. have been used successfully. This makes for a considerable saving in space and plant complexity, and the non-metallic construction is well suited to dyestuff filtration. Manufacture is an interesting example of the art of the cabinet-maker rather than the joiner, with well-fitting dowel pins (hardwood pegs) replacing the more usual screws to produce an all-wood construction (Fig. XVIII-3). The frames tend to warp and are not easy to make tight,

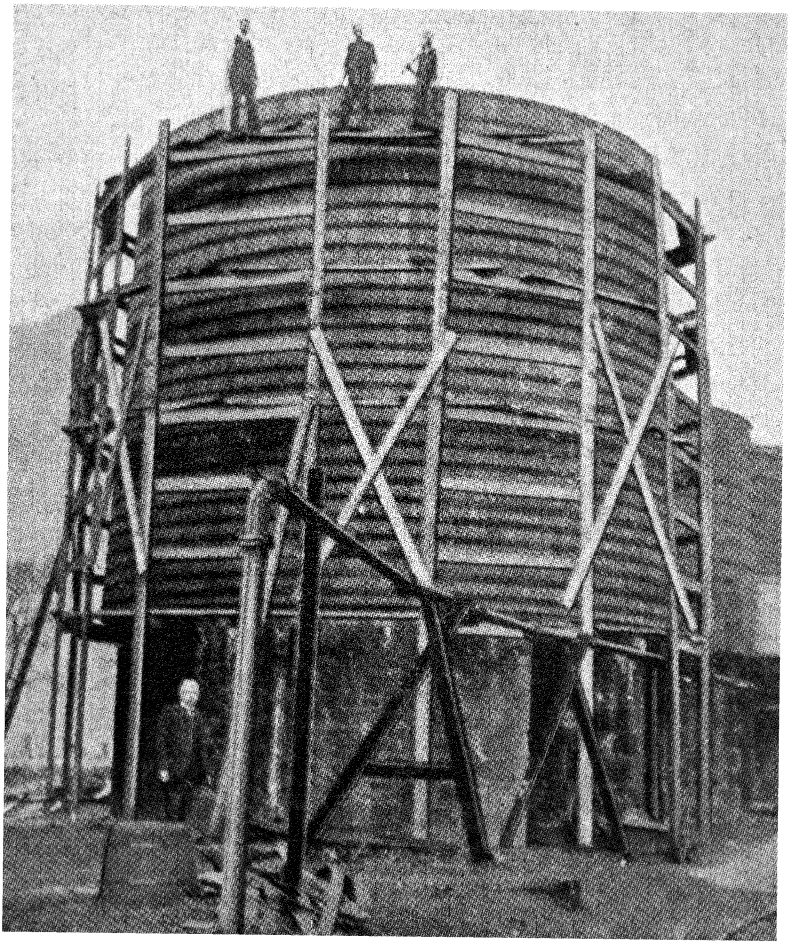


FIG. XVIII-2.—WOODEN VAT OF 115,000 GALLONS CAPACITY.

(Courtesy of J. McNicol & Son, Glasgow)

while subject, owing to intermittent wetting, to many forms of bacterial attack.

Perhaps the greatest bulk use of wood in the chemical industry is found in the construction of water-cooling towers. The shell can be in reinforced concrete (Fig. XVIII–4), but the special packing is invariably of wood, and modern practice inclines towards the all-wood construction of Fig. XVIII–5. Metal or concrete substitutes would probably be less durable, and will give a much greater foundation load. Redwood timber is always used for these towers in the U.S.A., as it has very little change in volume with varying moisture

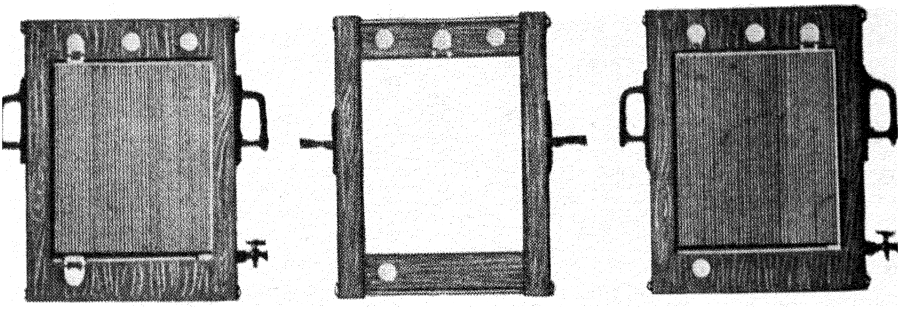


Fig. XVIII–3*a*.—Wooden Filter Plates and Frames.

(*Courtesy of Manlove, Alliott*)

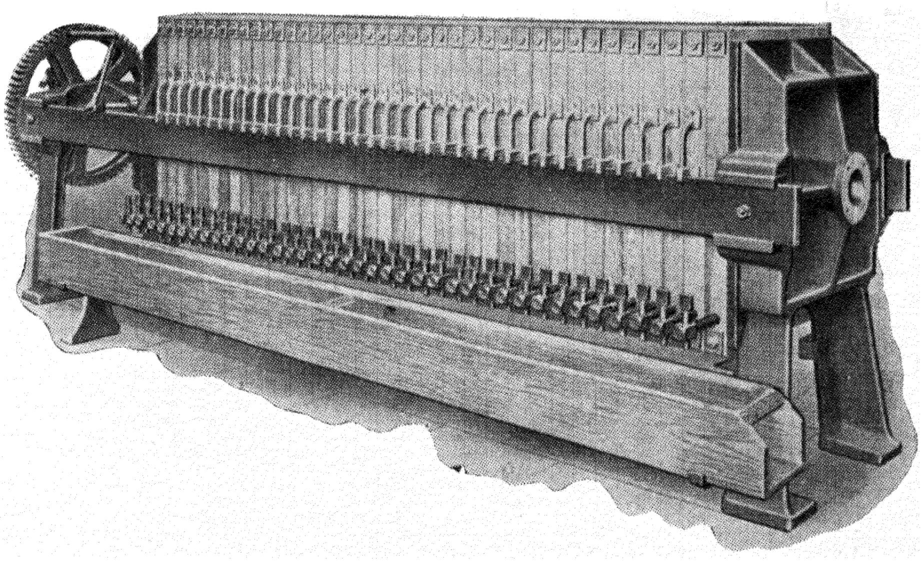


Fig. XVIII–3*b*.—Wooden Filter Press.

(*Courtesy of S. H. Johnson & Co.*)

content, is naturally resistant to decay, and can be obtained in sizes sufficient for the largest cooling units. Pitch-pine and fir have been used in this country, and no preservative treatment is necessary.

Certain types of wood—bamboo, hickory, spruce—can be obtained in the form of flexible rods which do not suffer from "fatigue" when put under rapidly varying stresses. They have been used as an alternative to steel springs in the support of screens for size separation. Pump rods for artesian wells are made from these and other woods, notably elm. Wooden pipes, built up from slats in the same way as a vat, are still being made for some purposes, such as conveying natural waters in bulk when iron contamination is to be avoided.

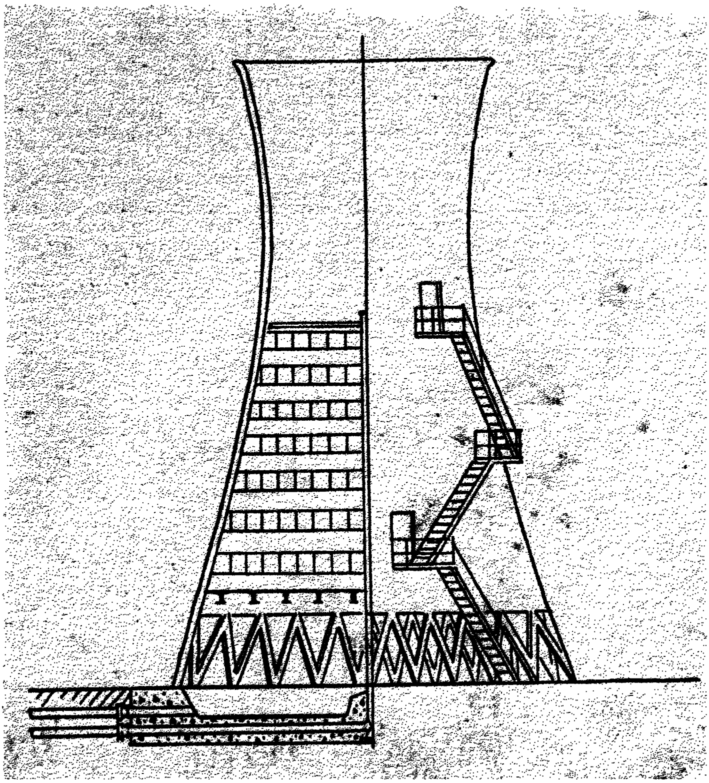


Fig. XVIII-4.

Wooden floors are, of course, quite common in all industrial buildings, and are the most comfortable type of floor for manual workers. The output from a group of plant operators can sometimes be increased by 20% if a change is made from concrete to wood as a working floor. On the other hand, resistance to chemicals and to wear combined is not satisfactory, and it is best to avoid wooden floors in most chemical plant. When used, a wooden floor should ideally be of rift-sawn planks, and the harder and heavier woods of high chemical reactivity are much more resistant to wear (Fig. XVIII–6).[6, 12] A hardwood floor resists oils and fats very well, but tends to give a very slippery surface. Lignum vitae, a very hard, heavy wood, has been used for submerged wooden bearings and is said to be acid-resistant.

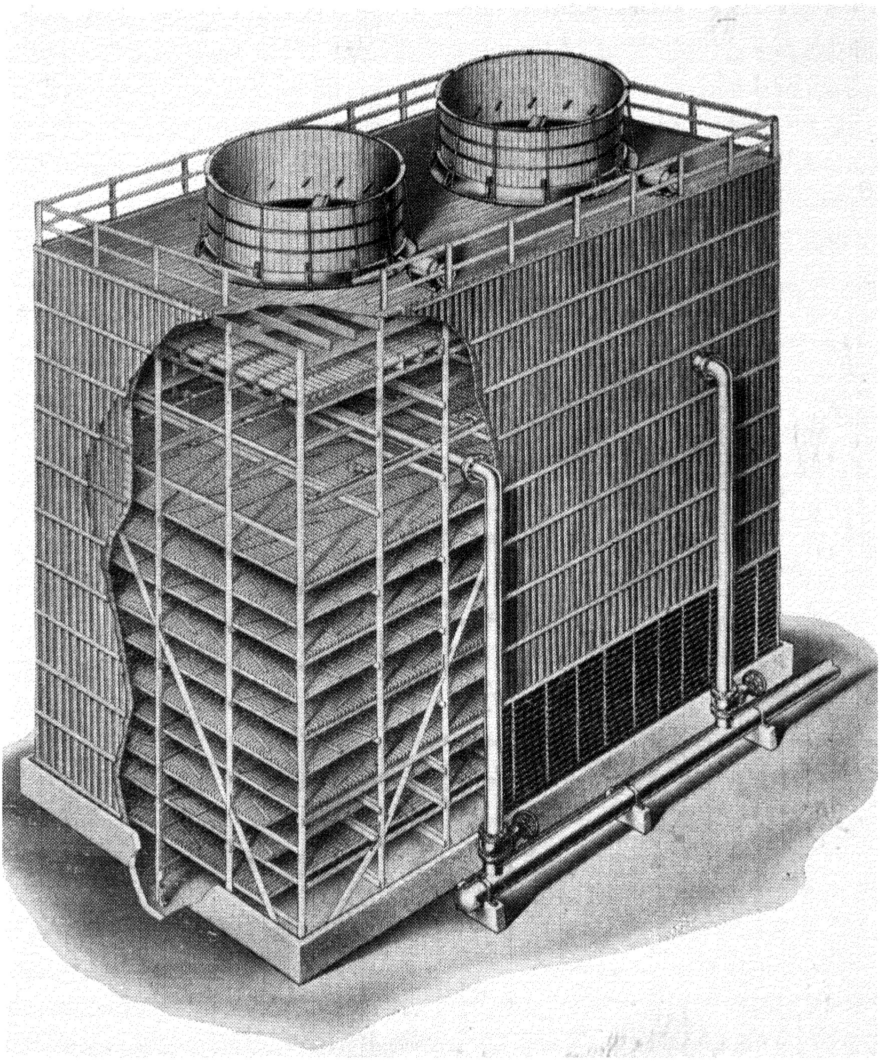


Fig. XVIII–5.—Internal Construction of Wooden Water Cooling Tower.

(Courtesy of Fluor Corporation of Los Angeles and Head Wrightson of London)

RESISTANCE TO CORROSION

A vat built from redwood, pitch-pine, or cypress will resist boiling 1% sulphuric acid, warm 5%, and cold 10% acid indefinitely. Hydrochloric acid is slightly less active and so is phosphoric, so that 20% solutions of both these acids can safely be stored in wood when cold. The use of wooden vats for diazotisation processes has already been mentioned. Here a mixture of nitrous and hydrochloric (or sulphuric) acid, kept at below 5° by intensive cooling, does not affect the wood, which in turn has no effect on the delicate colour shades required. The diazo solutions are filtered, as are the final colours, in wooden filter presses, using wool or polyvinyl chloride filter cloths and a hard-lead pumping system. Contact with metals for any prolonged period is thus entirely avoided. Despite the success of wood in this particular case, nitric and nitrous acids should not normally be handled, or any other strongly oxidising agent in solution. It was concluded many years ago that pitch-pine and Burma teak were the best woods for acid-storage vats.[7] Dilute organic acid solutions can easily be contained in wooden plant as wide use in fermentation plant demonstrates.

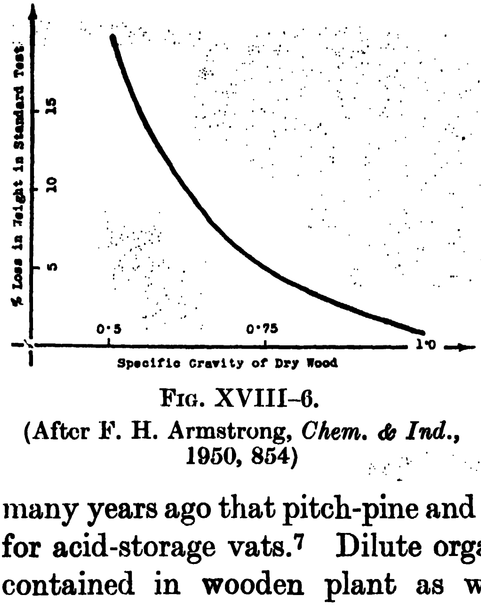


FIG. XVIII–6.

(After F. H. Armstrong, *Chem. & Ind.*, 1950, 854)

Acid fumes in moist air are conveniently led through wooden ducts and washed by water sprays in wooden towers. This usage is typified by the treatment of fumes from superphosphate "dens" containing hydrochloric, hydrofluoric, sulphurous, and sulphuric acid. The fume vents are in wood, with wooden washing towers, though the fans and sprays are in hard lead. A small plant making dilute sulphurous acid for corn-steeping was made entirely in wood, with the exception of a brick sulphur-burner, and gave excellent service over more than ten years.

Caustic alkali solutions all attack wood, and there is no need to use it where steel can give complete satisfaction. Nevertheless, when all metallic contamination must be avoided, dilute alkalies can be handled. A 10% solution of sodium carbonate has little action even at boiling-point, and a pitch-pine vat used in an emergency for hot (2% NaOH, 20% Na_2CO_3) solution continued in service for over a year without serious disintegration. Ammonia solutions are inert at ordinary temperatures, and a board-packed scrubber used for removing ammonia from coal gas lasted for over forty years, when the cast-iron plates of the tower were rusted to paper thinness in places. The board packing was in excellent condition, and could have been built straight into another scrubber. On the other hand, it has been suggested that bicarbonate solutions formed by over-softening water destroyed the packing of a cooling tower. This may have followed the course of bacterial decay following the leaching out of protective acids. The same effect has been noted with chlorine-bearing water overgenerously treated to prevent the growth of algae in cooling systems. Neutral salt solutions have no apparent action, either hot or cold, unless so concentrated that they commence to have a dehydrating action, but it would be clearly undesirable to impregnate a vat with such strongly oxidising agents as sodium nitrate.

IMPREGNATED WOOD—FIREPROOFING AND PRESERVATION

It is possible to "fireproof", or rather render fire-resistant, by a wide variety of treatments, ranging from simple lime-washing to impregnation with sodium silicate or ammonium phosphate. Curiously enough, pressure impregnation with creosote oil raises the primary ignition temperature from 200–250° up to over 550° C. The fireproofing also checks, to some extent, the normal tendency to decay. Real preservation, however, in wood exposed to wind and weather, can only be attained by heavy creosoting.[8], [9] The ordinary creosote can cause contamination of solutions, and special coal tar fractions should be used.[10] If these are applied under considerable pressure a "niggerised" wood is obtained which is supposed to have a considerably enhanced resistance to all chemicals. Whether the increased resistance is worth the additional cost is doubtful, as it is difficult to ensure that the characteristic microstructure of the wood has been completely sealed off. Sulphur impregnation, tried as a means of acid-proofing, has not been very successful, but a resin filler, polymerised *in situ*, appears to have more protective effect. The wood structure is retained, as distinct from woodmeal-filled moulding powders, and an interesting combination of wood strength and resin resistance is theoretically possible. At least 30% of the pure resin would be required if all the pores are to be filled, and it is a little doubtful if the prepared wood-resin could be made and sold at an economic price.[11]

Polymer-filled wood should be distinguished from the resin-bonded plywoods, made up from several layers of thin (0·2–1 mm.) wood, interleaved and impregnated with a suitable thermosetting polymer, and cured under pressure. This plywood can be made with a mechanical strength fully equal to its constituent wood laminae, and with no grain difficulty. It is possible to build up sections of almost any size, as the history of aircraft construction shows, and the material is admirably suited to the construction of fume ducts where lightness is a great advantage. These plywoods have come to the fore as a substitute for heavy timbers in the last few years; the older glue-bonded plywoods could be broken down by moisture in the course of a week or so, and could never be exposed to outdoor conditions. With the gradual lessening in the supply of large timber, and realisation of the resistant qualities of properly bonded plywood, formed sections may come into larger use.

Woodmeal is widely used as a filler for moulding powders. It retains all the weakness of wood from a chemical standpoint, while the breakdown of cell structure has destroyed all fibre strength and made the meal even more susceptible to attack by any reagent. Woodmeal, then, is seldom used for any chemically resistant compositions, as will be seen in the next chapter.

REFERENCES

1. Campbell, W. G., and Bamforth, K. F., *J.S.C.I.*, 1939, **58**, 180.
2. Heyerdahl, T., "The Kon-Tiki Expedition", Allen and Unwin, 1951.
3. Handbook of Empire Timber, H.M.S.O., 1945.
4. Cartwright, K. St. G., and Findlay, W. P. K., "Decay of Timber", H.M.S.O., 1946.
5. Rudge, E. A., *Chem. and Ind.*, 1930, **49**, 697.
6. Armstrong, F. H., *Chem. and Ind.*, 1950, 854.
7. Alliott, E. A., *J.S.C.I.*, 1926, **45**, 463 T.
8. Bennett, R. G., *Proc. Chem. Eng. Grp.*, 1940, **22**, 40.
9. B.S. 144 (1936). See also B.S. 1282, 913.
10. McNeil, D., *Chem. Tr. Jour.*, 1952, **130**, 1517.
11. *Chem. Met. Eng.*, 1944, **51** (5), 132.
12. "Floor Finishes for Industrial Buildings", National Building Studies No. 11, H.M.S.O., 1952.

An excellent bibliography on the use of wood in chemical plant is set out by W. G. Campbell and D. F. Packman, "Materials of Construction", p. 50.

CHAPTER XIX

PLASTICS AND RUBBER

THESE organic polymers are closely related and should form ideal materials for plant or plant lining when handling inorganic compounds, while a really inert high polymer will withstand all organic solvents in addition. When the first thermosetting plastics or resins appeared some thirty years ago and their chemical stability was realised, it was hoped that a transparent, corrosion-proof chemical plant would soon be available. Despite a promising beginning—transparent polymers of fair stability were available in the mid-'twenties—development has been relatively slow.

One primary difficulty with chemically synthesised polymers has been the cost. Taking simple phenol-formaldehyde as an example, a pure phenol will cost (1952) some 18 pence per pound, and formaldehyde a little less. These must be combined, mixed with a filler, and "cured"—polymerised to a final state—in heated moulds under pressure. ("Contact" resins simplify this final treatment.) For corrosion resistance the filler cannot simply be woodmeal, the most usual constituent of industrial moulding powders. It must be a good asbestos fibre or glass cloth, either of which can be nearly as expensive as the resin. In the circumstances, a finished plant section can hardly cost less than 2*s.* per pound, or perhaps three times the cost of steel plant. It is not possible to work with crude materials in the manufacture of stable polymers, as the polymerisation would be checked and the finished material rendered much more reactive. The alternatives to a phenol-formaldehyde resin are many, but they are not less expensive, and generally more costly. In the circumstances, chemical plant made from artificial resins is never likely to be cheap.

Again, the strength of a polymerised organic compound is low. Figures given later in this chapter suggest an ultimate tensile strength of, at most, 10,000 lb./sq. in. for an unreinforced polymer in forms which can be built direct into pressure-resisting vessels. Taking polyvinyl chloride ("P.V.C.") as typical, a safe stress of about 1500 lb./sq. in. can be assumed. Now if a pipe-line of 2 in. diameter (internal) is to carry fluids at a pressure of 500 lb./sq. in., the wall thickness is given by the standard "Thin Wall" formula as 0·33 *inches.* Taking for mild steel the conservative safe stress of 10,000 lb./sq. in., wall thickness for a similarly stressed pipe would only be *0·05 inches.* If the relative densities of polymer and steel are taken as 1·39 and 7·8 respectively, the weight of pipe per foot run will be: Polyvinyl chloride *1·46 lb.*; steel *1·09 lb.* The actual weight of polymer required for a given duty is thus greater than with steel, despite the very large difference in density. It should be added that for many purposes rigidity of wall is of more importance than strength, and a light P.V.C. section can often replace a much heavier steel part. It would also be preferable to compare "P.V.C." with lead, as this metal is the real alternative to the polymer.

The obvious answer to this problem of strength is to develop a reinforcing material which can be imbedded in the polymer during manufacture and provide all the strength required. It will be necessary to ensure that the reinforcement is covered completely by the resin, or that it is itself resistant to corrosion. Glass fibres seem ideal for the purpose, except when hydrofluoric acid is being handled. As mentioned previously, glass in fibre form has a very high tensile strength, and it is easy to prepare reinforced polymer sheet with an ultimate tensile strength of 50,000–60,000 lb./sq. in. Normal working strengths are much lower,[1] however, and it would appear that the needs of corrosion resistance call for weaker reinforcing than the fine and rather reactive glass fibre. Another trouble is also encountered, as with the paper- or cotton-reinforced plastic material used for mechanical parts. The reinforcing is in layers, with the polymer acting as a binder. Grain structure, as in wood, is produced, with a much greater strength along than across the grain. This necessarily interferes with the fabrication of complicated parts, as a glance at Fig. XIX–1 will show. A wrapped pipe can easily be made in straight forms, but a bend must either be sweeping with a large radius, or built up by moulding to a relatively clumsy form. Tees and elbows can be "cast" into shape by using an unpolymerised mixture with a glass-wool filler and setting in moulds, but such shapes can only have the strength of unreinforced polymer. Nevertheless construction of this kind has made possible such complicated plant forms as are shown in Fig. XIX–2.

The polymer base of these reinforced sections is normally thermosetting, and in a pure form would be rather brittle and subject to shrinkage stresses. This is overcome by the use of a "plasticiser", which usually takes the form of a co-polymer with more elastic properties. Now this will modify the mechanical characteristics of the polymer to any desired extent, but will in general increase reactivity with many chemicals. For this reason, little plasticiser is incorporated, and the finished section tends towards brittleness.

The alternative to building a complete plant from reinforced sections is to use the polymer only as a liner for some metal part, usually of steel. Thin layers formed from suitably joined sheets, or even polymerised *in situ*, can absorb the stresses of setting and present a uniform, corrosion-resistant surface. This permits the use of rubber-like polymers, which may be most resistant, especially to abrasion, and also allows of considerable economy in the use of expensive materials. The lining must not be too thin, however, and painted coats are normally unsatisfactory because of pinholes. These or superficial damage may lead to local penetration and corrosion, followed by a stripping of the entire film. Such stripping is made easier by poor adhesion between metal and polymer, the most chemically inert materials being particularly unsatisfactory in this respect. As the substances handled in polymer-lined plant are often extremely corrosive, it is necessary to ensure that no spillage over unprotected metal occurs. As any chemical plant operator knows, frothing or boiling over of a reaction vessel is among the most

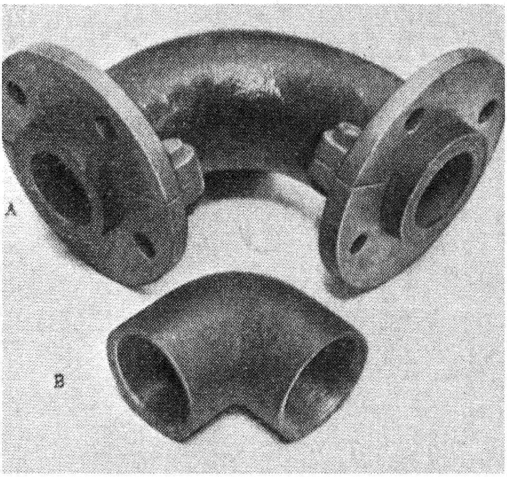


FIG. XIX-1.—REINFORCED POLYMER (A) AND MALLEABLE IRON (B) PIPE FITTINGS OF EQUAL CARRYING CAPACITY.

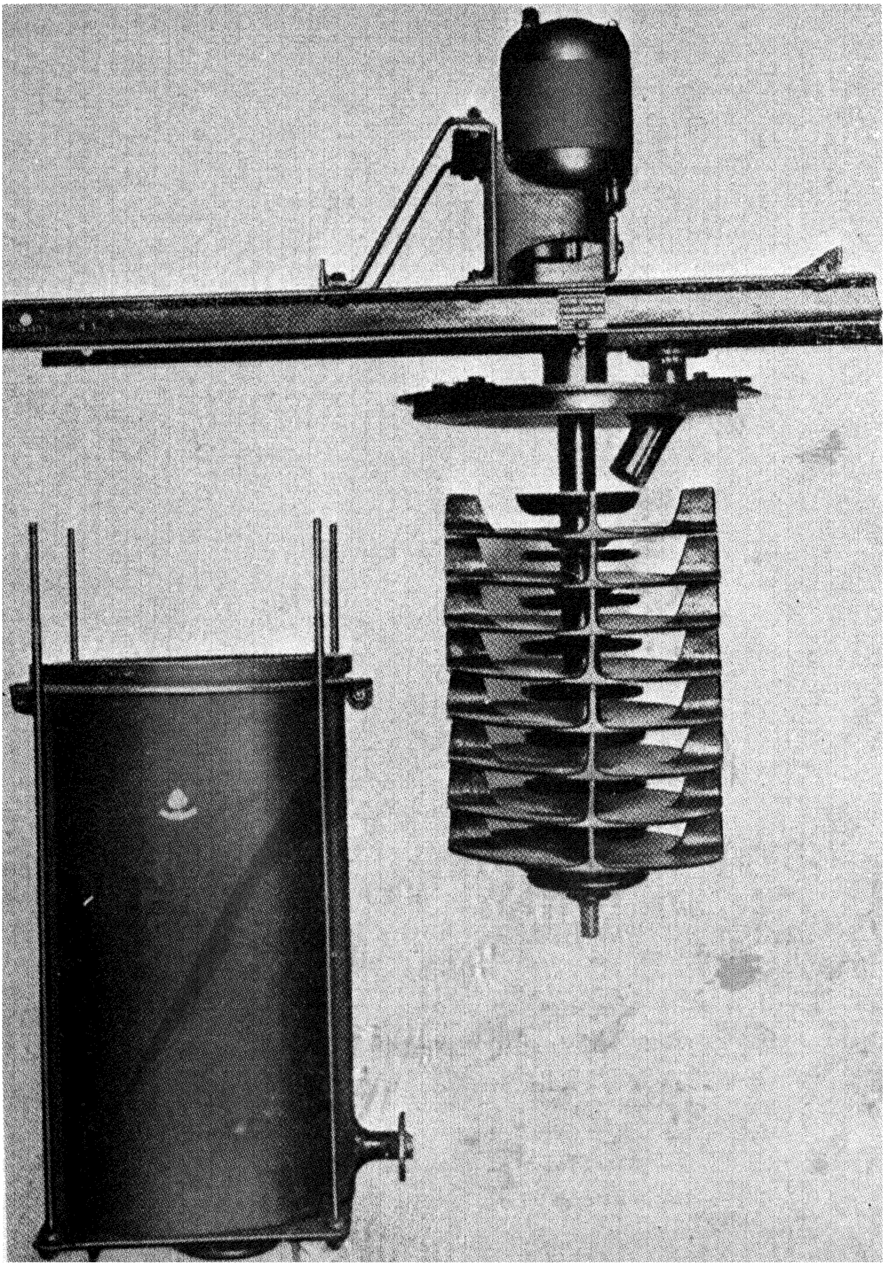


FIG. XIX-2.—REINFORCED RESIN PLANT. UNIT FOR TREATING MERCURY WITH ACID.

(Courtesy of Kestner Evaporator & Engineering Co.)

common of mishaps, and it is not easy to protect the outside of a lined vessel against such an eventuality. For these various reasons, reinforced plastic plant sections have been developed side by side with polymer lining for steel plant, and in neither case has any widespread adoption of such plant taken place.

REINFORCED THERMOSETTING PLASTIC PLANT SECTIONS

As indicated above, these are made by impregnating layers of woven cloth (or fibre masses) with the liquid monomer, and then shaping to the final form and curing under pressure at about 100° C. The original resins were of the phenol-formaldehyde type, but this has been largely substituted by furfuryl alcohol and furfuraldehyde polymers, which are somewhat more temperature-resistant and of about the same chemical stability. Attempts are now being made to introduce complicated polyester resins, which can be "cured" at lower temperatures and without any need for pressure. The strongest form generally available has been made up from compressed cloth or paper layers, and a wide range of finished forms is sold under the trade name of "Tufnol". Mechanical properties have been covered by specifications,[2] and this particular material has been developed for general engineering rather than for chemical plant work. Somewhat weaker grades, sold in this country as "Keebush",[3] on the Continent as "Haveg", and in the U.S.A. as "Permanite", have been designed for resistance to chemicals. The essential properties of Tufnol, Keebush, and Haveg from a mechanical standpoint are set out in Table XIX–1 below.

TABLE XIX–1

Property	Tufnol	Keebush	Haveg
Ultimate Tensile Strength along grain (lb./sq. in.)	10,000–22,000	2500 (can be made up to 15,000)	2000
Crushing Strength:			
Grain upright (lb./sq. in.)	29,000	10,000	11,500
Grain flat	48,000	—	—
Specific Gravity /water at 4°	1·36	1·60	1·6
Thermal Conductivity B.Th.U./(sq. ft.)(hr.) (° F./in.)	2–3	2·4 up to 7·2	4·8
Coefficient of Linear Expansion	$(1\cdot4\text{–}3\cdot0) \times 10^{-5}$/° C.	$1\cdot5 \times 10^{-5}$/° C.	$1\cdot2 \times 10^{-5}$/°C.

Tufnol and allied compositions can be bought in most standard angle and sheet forms, with some size limitations, and can be cut, machined, and threaded like a metal. Tufnol gear-wheels are widely used in "silent" machinery, and the resistance to most aqueous solutions, if dilute and cold, is quite satisfactory. Normally Tufnol should not be exposed to concentrated and active reagents, nor to temperatures above 80°, though a special form ("Asp") is stable up to 165°.

The chemically resistant plastic forms are weaker, but can still be machined to carry a coarse thread or give a faced joint between two pipe lengths, as shown in Fig. XIX-3. The hot-pressing used for Tufnol sections cannot always be applied to more complicated plant forms, which accounts in part for the lower mechanical strength. Large vessels, up to 8 ft. in diameter and 10 ft. high, can be moulded in one piece, but need reinforcing with steel hoops and wooden staves, as shown in Fig. XIX-4. Still larger tanks of rectangular section can be built up from faced pieces, clamped together in angle-iron frames. The surface is hard enough (Brinell 18–20) for erosion and shock resistance, and such tanks are an alternative to the conventional A.R.-brick-lined concrete.[17] It is possible to make the moulded form strong enough for centrifugal pump impellers, while the agitator of Fig. XIX-2 is an indication of stiffness and erosion resistance. The maximum working temperature for phenol-formaldehyde and furfural-based resins is about 130°–140°, but the limit thus set may be raised by changes in the resin base. The newer polyester resins are claimed to have working temperatures as high as 200°, and silicones can be used up to 400°.[21]

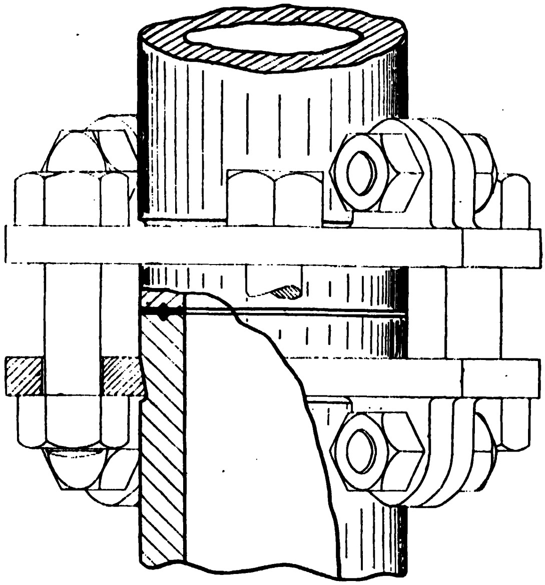


FIG. XIX-3.—JOINT FOR KEEBUSH PIPE.

(Courtesy of Kestner Evaporator & Engineering Co.)

Heat-exchange plants can be built in Keebush and related materials, but suffer from the low thermal conductivity of, at most, 7·2 B.Th.U., etc. A 1-in. bore pipe would have a wall thickness of about $\frac{1}{8}$ in., which gives a wall coefficient of 58 B.Th.U./(sq. ft.)(hr.)(° F.). Heat flow will be slow even if all the other resistances are negligible, as the low working temperature means some restriction in temperature difference. In order to overcome this difficulty,

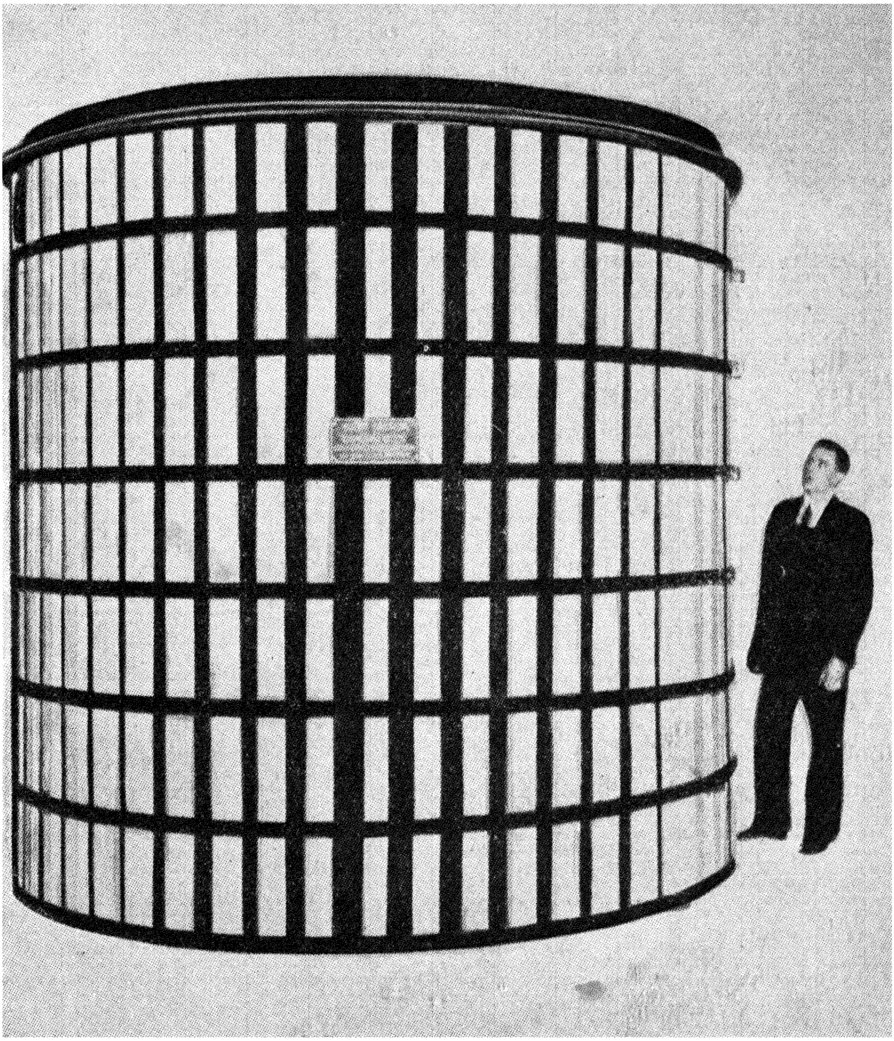


FIG. XIX–4.—8 FT. 0 IN. DIAMETER STORAGE TANK.

(Courtesy of Kestner Evaporator & Engineering Co., Ltd.)

tional tube-and-shell heat interchanger, as shown in Fig. XIX-5. The tubes can be threaded, but it is best to rely on cemented joints using a thermosetting cement of suitable composition. The material is as brittle as glass or silica, and a special block form of heat-exchanger has been designed to overcome this disability (Fig. XIX-6). The graphite block is drilled with rows of holes in two directions at right angles, and a very compact form of heat-exchange surface is obtained. Carbon or graphite tubes can be

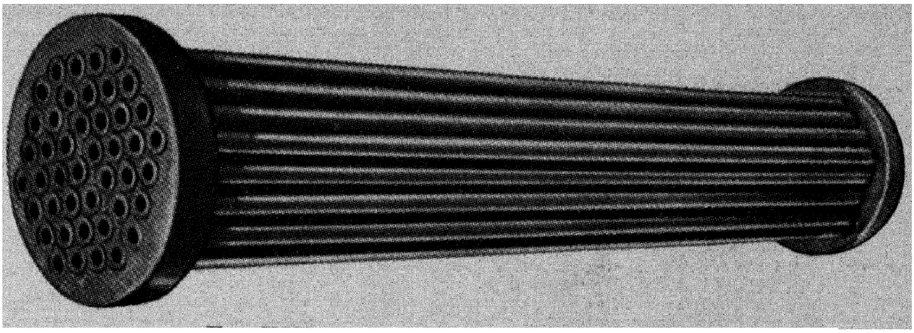


FIG. XIX-5.—HEAT EXCHANGER IN CARBON.
(*Courtesy of Morgan Crucible Co.*)

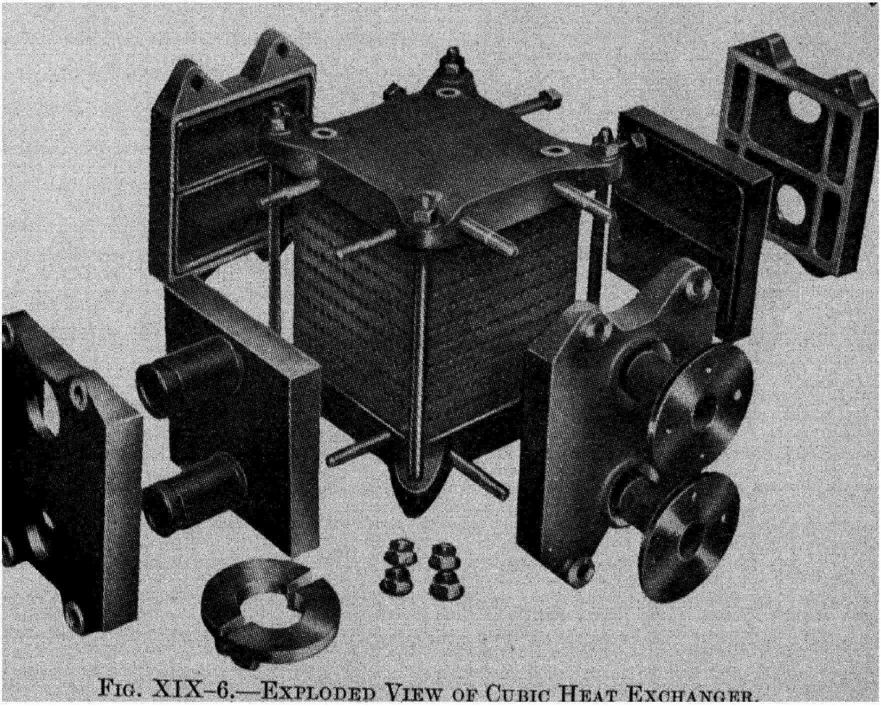


FIG. XIX-6.—EXPLODED VIEW OF CUBIC HEAT EXCHANGER.
(*Courtesy of Powell Duffryn Carbon Products, Ltd.*)

combined with Keebush to give a conventional design of climbing film evaporator, and plate-type heat-exchangers in graphite have been built.[4] Valves to match the graphite tubes are now available (Fig. XIX–6a).

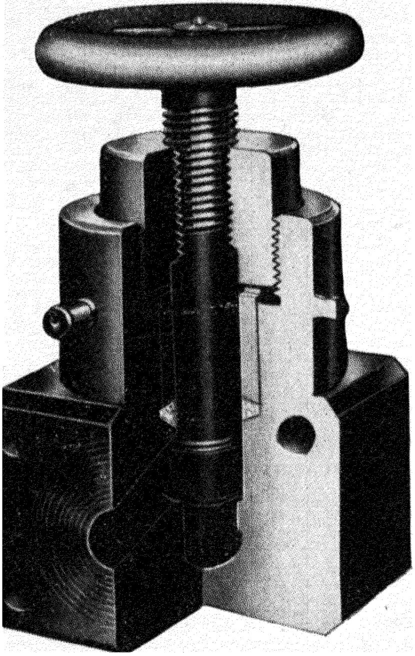


FIG. XIX–6a.—VALVE IN KARBATE.
(*Courtesy British Acheson Electrodes, Ltd.*)

The normal carbon plant unit would be bought direct from the makers, with no need to do more than connect up to the various pipe-lines, but if plant is built up *in situ* it will almost certainly be cemented, using the resin cement mixtures already mentioned in the discussion on acid-resisting brickwork. Probably the most frequent use will be in the lining of tanks with carbon tiles. These, in either amorphous carbon or graphite, can be obtained in sizes up to 15 in. square, and can be set in graphite-filled resin cement straight against the metal wall. As the coefficient of thermal expansion is from a half to a third that of steel, large differences in temperature should be avoided, but the high thermal conductivity of the tile offsets the possibility of cracking.

THERMOPLASTIC POLYMERS

These materials have a low maximum working temperature, but are stronger and less brittle than the thermosetting compounds dealt with above. The gradation of properties from a rigid polymer of the phenol-formaldehyde class, through the thermoplastic polymers to the fully flexible rubbers is gradual and no sharp lines of demarcation can be drawn. One of the newer polyester compounds can have a quite rigid structure at ordinary temperatures, but becomes quite soft at temperatures around 250°, while of course rubber itself can be frozen to a brittle solid at temperatures below 0° C. Polymers of the type that gradually lose strength as the temperature rises from 50° to 150°, in general as a reversible change, are classed as thermoplastic. Those most commonly used for chemical plant are set out in Table XIX–3.

TABLE XIX–3

Properties of:	Polythene	Polyvinyl Chloride	Perspex	Teflon
Specific Gravity	0·92	1·39	1·19	2·2
Ultimate Tensile Strength,* (lb./sq. in.)	1750	8000	8000	2000–4000
Thermal Conductivity, B.Th.U./(sq. ft.)(hr.)(° F./in.)	2·4	1·2	1·2	0·6
Brinell Hardness	2·0	15	18	2
Thermal Expansion, (in./in. ° C.) $\times 10^{-5}$	20	8	9	6
Maximum Working Temperature, ° C.	55-75 (Variously Stated)	60	70	300

* Creep rates may be high.[22]

These four polymers have been fabricated into units of chemical plant and used with success. A vast number of alternative compounds have been made up for other industries, but have not yet been applied in the manufacture of chemicals.[23]

Polythene (polymerised ethylene), P.V.C. (the polyvinyl chloride), and Perspex (polymethyl methacrylate) are the three most commonly found, with P.V.C., perhaps the cheapest, as the most widely used. Teflon (tetrafluorethylene) costs at the present time about 5*s.* an ounce, and obviously cannot be used in large quantities. All four are available as granules for hot-pressing, or as sheets, tubes, and threads. The bulk material can be machined quite easily provided that the cutting tool is cooled with an air-jet, while P.V.C., or Perspex, is hard enough for screw-threads. Teflon gives traces of fluorine compounds when carelessly cut, but in normal practice these are much too small to be detected. Welding, using a jet of hot gas from some form of heating torch and a rod of the polymer, is now a well-established technique with both P.V.C. and polythene.[5, 18] Perspex shapes can be cemented together using a number of proprietary cements, or even painting the edges with chloroform and pressing into position. This latter is not used for severe service conditions, but rather where it is required to observe the operation of some plant section or utilise the optical transparency of the polymer. Welded joints in P.V.C. or polythene are fully as strong and chemically resistant as the rest of the plant.

With these welding methods vessels of very considerable size have been built up. Tanks in P.V.C. for acid-handling (HF and HNO_3) of 500 gall. capacity have been made, while long lengths of 2-ft. diameter ducting have given excellent service (Fig. XIX–7). Pipe lengths are available in P.V.C., the closely allied polyvinylidene chloride, and in polythene. The first two can be extruded into long continuous pipe lengths, capable of being coiled like rubber hose, while specifications[19] have just been published for polythene tubing. All three are rather soft, but the polythene can be threaded and P.V.C. is strong enough to make centrifugal pumps or gas fans. Valve diaphragm for such valves as the well-known Saunders form have given every satisfaction in the control of acid flow. These plastic pipes are now replacing lead or glass as the all-purpose corrosion-resistant conduit in acid plants.

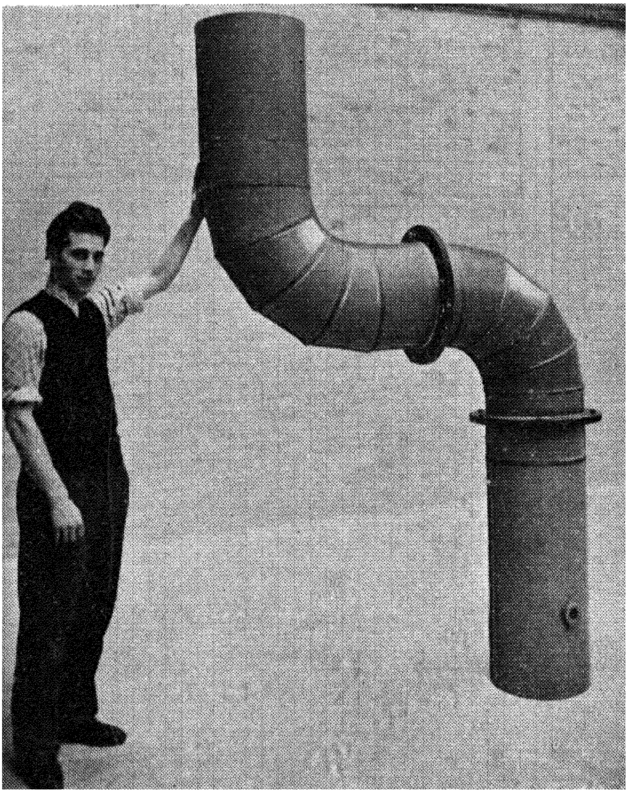


FIG. XIX–7.—PVC TUBING.

(Courtesy of Rediweld, Ltd.)

Polythene is obviously well adapted for linings inside steel vessels, especially if some method be devised for securing good adhesion between metal and polymer. The present form of polythene lining is loose and attached by studs, which are afterwards welded over by polythene covers, as in the older lead-lining practice. P.V.C. sheets, on the other hand, can be firmly cemented to the metal, or to concrete and wood, a number of proprietary cements being available. When lining metal tanks a "hot-process" cement is applied to the preheated wall, and sheets of P.V.C. are rolled into place. At the wall temperature these deform readily to follow plant contours and the sheet edges are then welded together. If changes in temperature are expected, a somewhat thicker cement layer allows the formation of an elastic undercoat and holds the top P.V.C. sheet firmly in place. Concrete tanks and wooden vats can be lined in the same way, but the cement is cured by infra-red radiation. Wooden vat staves dry out and shrink, as usual, behind these impervious linings, and it is necessary to reinforce the joints.

The only advantage of Perspex over P.V.C. appears to lie in the optical transparency, which for infra-red and ultra-violet light is at least as good as normal glass.[6] Certain forms of algae requiring irradiation have been grown under Perspex covers or in solutions pumped through Perspex pipe. Though definitely weaker and less resistant than welding, cemented joints allow transparency to remain unimpaired, and most Perspex plant is assembled in this way.

Teflon, most chemically resistant of all polymers so far manufactured, has the resultant disadvantage that it is almost impossible to obtain adhesion to any other surface. Teflon linings, like polythene, must be loose envelopes at best, and while some hopes have been expressed that a cement for polythene can be found, the Teflon seems very intractable. As a result, a slightly more reactive derivative, chlor-trifluoro-ethylene or Kel-F, has been manufactured and can be induced to adhere more effectively. High cost stands in the way of wide adoption, as these fluorinated compounds have remarkable chemical resistance and can be used to temperatures at least as high as any thermosetting resin. The principal use so far has been in the manufacture of gaskets and valve sections for strong acid plants. The low mechanical strength can be bolstered by using glass-fibre-reinforced laminates, and a gasket cut from such a complex can withstand boiling nitric acid containing chlorine or other halogens. It is resistant to erosion, has self-lubricating qualities and would appear ideal for gland packings.

WOVEN CLOTH

The four thermoplastic polymers described above can all be obtained in thread form, as can also Nylon, a polyamide. Ordinary textile processing will give a cloth which can be used in filtration, having high corrosion resistance and some characteristic properties in addition. The normal filter cloths of chemical practice have been made from wool or cotton, and the earlier artificial fibres showed no improvement on these traditional materials. Glass fibres, introduced some fifteen years ago as the ideal acid-filter media, were shown to be very brittle under stress and rather reactive. With the development of P.V.C. fibres,[7] generally copolymerised with such additions as vinyl acetate (Vinyon) or acrylonitrile (Vinyon N), a new filter cloth could be woven which was unattacked in the cold by all but the strongest acids or alkalies. It was also very strong and the fibres did not swell when wetted, so that blockage of filtering pores was less frequent than with cotton or wool. Nylon fibres had something of the same non-swelling characteristics, and Nylon cloth was found to be more resistant to alkalies than the P.V.C. complexes. The more important properties of these fibres are set out in Table XIX-4.

TABLE XIX-4

Fibre:	Wool	Cotton	Vinyon	Polythene	Nylon
Properties					
Tensile Strength, lb./sq. in.	20,000	60,000	60,000	20,000	70,000
Maximum Temperature, ° C.	Varies, but about 100°		70°	70°	200°
Resistance to:					
Weak Acids	Good	Poor	Good	Good	Fair
Strong Acids	Poor	Bad	Fair	Good	Poor
Weak Alkalies	Poor	Good	Good	Good	Good
Strong Alkalies	Bad	Poor	Good	Good	Good
Organic Solvents	Good	Good	Fair	Fair	Fair

It will be appreciated that the above table represents average behaviour, especially in the case of natural fibres.

In such an important industrial field, development is very rapid, and new forms of artificial fibre appear almost every year. For instance, Terylene, a polyester fibre, may have as good a temperature resistance as Nylon, and a better acid resistance. It has been used in filtering calcium sulphate from hot phosphoric acid.[8]

Corrosion Resistance

Corrosive attack on polymers does not take the usual form of surface atom loss, with the possibility of inhibition by deposition. The reacting solution rather tends to diffuse into the actual solid structure and weaken the molecular bonding. First signs of attack are not weight loss, but rather swelling and gain in both bulk and weight. Such a swelling can, for instance, loosen the bond between polymer lining and backing metal, or set up stresses in a homogeneous structure which can break the polymer wall at a weak point. For instance, a polymer lining can crack at the "water line", an analogous effect to stress corrosion in metals (?), while clear Perspex grows opaque as droplets of solvent force their way between the molecular layers.

Following on this, it is clearly undesirable to handle any organic solvents in resin plant. It is true that plain hydrocarbons and the lower alcohols have little or no action on thermosetting resins, though they soften most thermoplastic polymers slightly. Chlorinated solvents and the various general solvent agents developed for the paint industry will probably have some slight action on any polymer. Except in the rare contingency of a very active acid and an active organic solvent being mixed together, it is improbable that resin plant will be required to handle these organic liquids, most of which have little action on metals.

The resistance of all these synthetic polymers, except Nylon, to all strengths of hydrochloric acid is absolute, though the working temperature range may be limited. Sulphuric acid solutions, with the same exception, are equally inert until a concentration above 60–70% H_2SO_4 is reached, when only Teflon is of any use. Nitric acid, in the same way, reaches a dangerous concentration at about 50%, though a P.V.C. tank has been used for 70% HNO_3/ 70% HF, cold,[9] with every satisfaction. A P.V.C. hose carried spent nitrating acid (10–20% HNO_3/50–60% H_2SO_4) for six months without signs of attack, and the air lifts of a nitric acid recovery plant, long constructed of glass, can now be made up in the much more robust and flexible piping of polythene or P.V.C.[24] Nylon cloths have been used for filtering hot *dilute* acid solutions, but the practice is no longer necessary with Terylene available. All moist halogens attack every polymer except Teflon, which has been widely used for gaskets in glass or enamel plant containing these very active chemicals. Dilute hypochlorous acid and bleaching solutions generally have little or no action on the thermosetting resins, furfural-based forms being particularly resistant. Neutral, feebly acid, or feebly basic salt solutions of any kind are freely handled in polymer plant,[10] the only restriction being in the working temperature. No metallic contamination can occur by plant contact.

Strong caustic alkali will disintegrate a phenol-formaldehyde-based resin plant, but good resistance to ammonia and basic carbonate solutions is easily obtained. Furfural-based resins are better than the older Baekelite and even the strongest caustic alkalies have no action on polythene, P.V.C., or Teflon. There seems little purpose, however, in using expensive resins for such solutions. They should be kept for extremely corrosive acids, in which circumstances the order of inertness would appear to be Teflon—Polythene—P.V.C.—Phenol-formaldehyde and Furfural-based resins—Perspex—Nylon. Teflon is only attacked by molten sodium and is one of the most inert compounds that can be visualised.

The cheapest organic polymers are those based on phenols or furfurals, costing some 2*s*. per pound, and the price of the others mounts steadily up to the very expensive Teflon. Relative prices change rapidly in this field and present indications (1953) suggest that P.V.C. in piping form is competing successfully with lead. The whole range of corrosion-resistant "plastics" widens every year. It may be that the slow development referred to in the opening paragraphs will be succeeded by rapid progress provided that the cost can be kept down.[20]

RUBBER

It is proposed to deal under this heading with both natural and artificial rubber. The basic natural rubber is a hydrocarbon polymer of peculiar structural form, and various attempts to synthesise a similar structure have only been partially successful. *Neoprene* is a polymer of chlorinated isoprene, *G.R.S.* a co-polymer of styrene and butadiene, *Butyl* a butadiene–butylene complex, and *Thiokol* an organic polysulphide polymer. A recent development in the chemistry of silicon has led to the preparation of *Silicone* rubbers, in which chains of Si–O–Si– replace those of carbon, but these are too costly for general use at present. It is a characteristic feature of natural rubber that it reacts with sulphur ("vulcanises") in such a way that all physical properties are profoundly modified. Characteristics of the more important of these rubber-like materials are set out in Table XIX–5, but it must be understood that these are only average figures for a large family of compounds in each case.[11]

TABLE XIX–5

Type of Rubber	Soft Unfilled	Carbon-Black Filled	Vulcanite (Hard Rubber)	Butyl	G.R.S.	Neoprene	Silicone
Tensile Strength lb./sq. in.	2500	4000	10,000	2000	2000	2000	500
Abrasion Resistance	Very good	Very good	Fair	Fair	Fair	Good	Fair
Maximum Working Temperature (° C.)	70°	100°	70°	120°		150°	250°
Minimum Working Temperature (° C.)	−60°		−20°			−50°	−60°
Coefficient of Thermal Expansion (in./in. ° C.)	$2{\cdot}1\times 10^{-4}$		8×10^{-5}				

Rubber in pure natural state, with no fillers and up to 5% of sulphur added, can be vulcanised by heating at 100°–140° C. to the soft rubber of commerce.* It can now show elastic deformation up to 5 times the normal length at ordinary temperatures, with an elongation at break-point of 900% and an ultimate tensile strength of about 2500 lb./sq. in. Elastic properties are modified profoundly by temperature change, and a brittle, crystalline solid forms around —70°, while the rubber can melt and depolymerise if heated above about 150° C. If the sulphur content is increased to 25–30%, and vulcanisation carried through as before until all the sulphur is taken up, hard rubber (ebonite) is formed, with an ultimate tensile strength of 10,000 lb./sq. in. and a trifling elongation at break. This form of rubber is quite hard enough to take screw-threads and cut like a metal. A whole range of intermediate forms, generally less satisfactory than either soft rubber or vulcanite, can be obtained by alterations in vulcanisation conditions.

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* Rubber hardness is measured by the Shore scale which notes penetration by a loaded point. A normal soft rubber will vary from 30 to 50 Shore, tyre treads are about 70, and ebonite tends towards 100 — the scale maximum.

The changes produced by sulphur are very marked, but other modifying agents or "fillers" can be incorporated into the rubber substance, the extension under load decreasing and hardness increasing as the filler content grows. The best resistance to abrasion is given by soft mixes, but one of the valuable properties of carbon-black filler is that abrasion resistance and elasticity are retained up to contents of 50% carbon. Thermal and electrical properties are altered, as well as chemical resistance, and no certain figures can be quoted for rubbers in which the original raw rubber has been attenuated to 20% or even less.

The merits of a soft rubber lining in resisting abrasion are well known. A cast-iron chute for ashes can be worn through to a depth of ½ in. over six months of use, while soft-rubber-lined chutes will not wear so much in as many years. Rubber-lined pumps for all sorts of slurries and rubber-covered fans for dust-laden air give excellent service. This abrasion resistance breaks down sharply, however, if the surface is tested beyond a certain point, and it is easy to strip rubber linings by sand-blasting. The amount of rapidly changing distortion that a rubber section will withstand is amazing. Rotary-pump impellers can distort to 50% of length with each revolution, rotating at 300 r.p.m., and thereby dispense with valve systems. Apart from this abrasion resistance, the chemical inertness of all forms of rubber to dilute aqueous solutions allows of wide use in linings, and rubber can be attached to metal so effectively that the bond is stronger than the actual rubber sheet (Fig. XIX–8). Details of the process are usually in the hands of the manufacturer, but a number of cements have been used, based on sulphonated oil or chlorinated rubber. These are painted on to the clean metal surface before applying the rubber sheets, very much as rubber adhesive is painted on to a punctured tyre. The sheets are then carefully rolled into position, taking care to exclude all air bubbles, and individual sheet joints welded by rubber solution. Normally a filled rubber sheet is used in unvulcanised form, and the complete section is vulcanised after lining. It is possible to use pre-vulcanised sheets—a procedure adopted with "pure" rubber, but adhesion is poor and temperature limitations are more marked than with vulcanisation *in situ*.

The best metals for lining with rubber in any form are steel and aluminium, but many brasses are just as good, and it is probable that any metal could be bonded if required by using some form of preliminary plating.[12] As shown in Table XIX–5, rubber in most forms has a higher coefficient of expansion than metal, but the coefficient is highest with the most elastic material, and very wide differences in temperature are not expected with this type of plant.

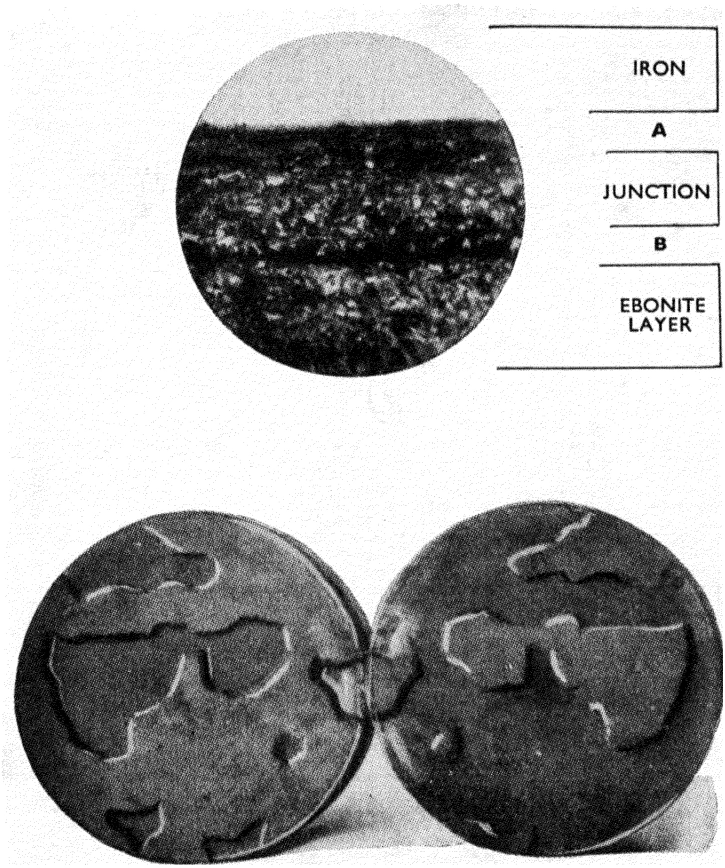


FIG. XIX–8.—ADHESION OF EBONITE TO IRON.

(Courtesy Nordac, Ltd.)

In the earlier years of rubber lining, emphasis[13] was laid on the need for vulcanising by boiling with water or brine. This made the task of curing a rubber-lined tank much simpler, but it would appear that most manufacturers prefer large vulcanising ovens when these are available (Fig. XIX–9).

It is necessary to ensure that the covering is complete, and a high-voltage electric probe is used to detect pinholes. A charged point (20,000 volts) gives a thin blue spark discharge on satisfactory covers, but the smallest crevice causes a heavy white flash. Rubber linings can be laid in wood or concrete tanks in the same way as with metal, but in such cases the lining mix must be adjusted for vulcanising by boiling water. A preliminary layer of rubber latex cement is generally applied, and this gives the advantage that surface irregularities can be smoothed over, and damaged containers given a new lease of life. N. Swindin, a pioneer in this field, describes the lining of wood, metal, and concrete tanks "in various stages of decay" by this latex cement, followed by rubber sheeting.[13] As with other waterproof linings, wooden tanks dry out, and the seams must be protected by a thick layer of latex cement, or cracks will form into which the rubber sheet is forced (Fig. XIX–10). A soft "pure" rubber lining should not be heated to above 70°, but the harder filled sheets, vulcanised into position, can be used constantly at 90° C. for long periods. Temperatures may reach 130° for short intervals, at any rate with some mixes, but the manufacturers'

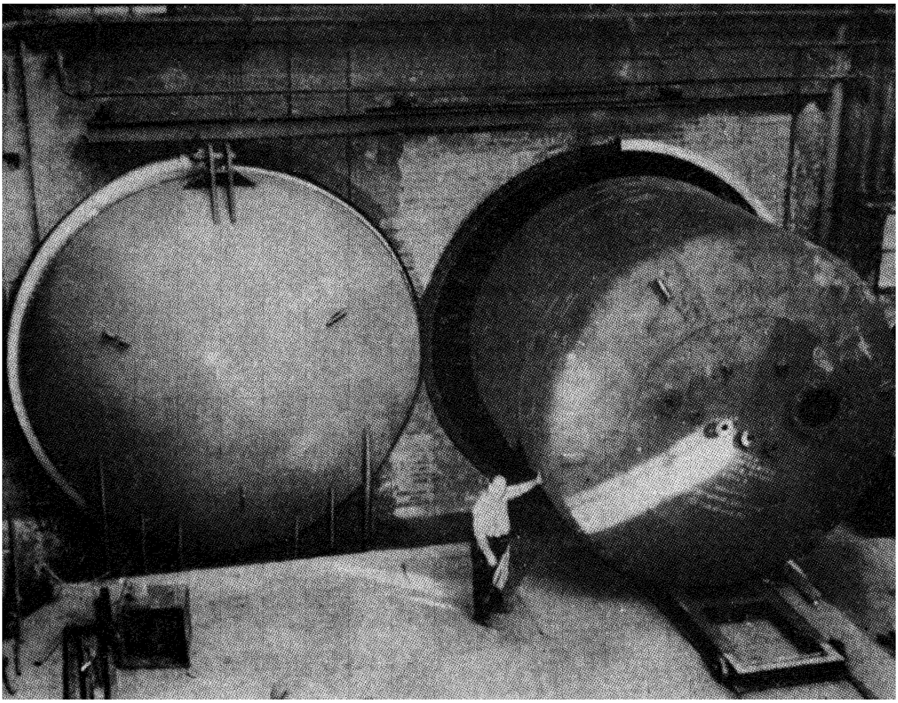
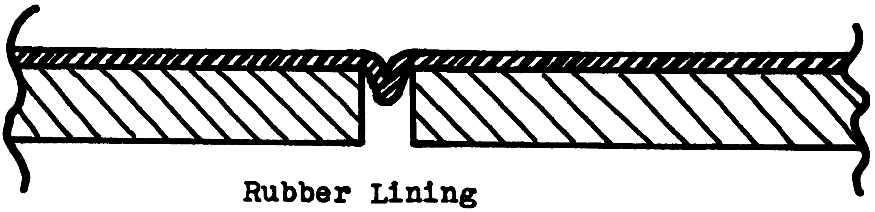


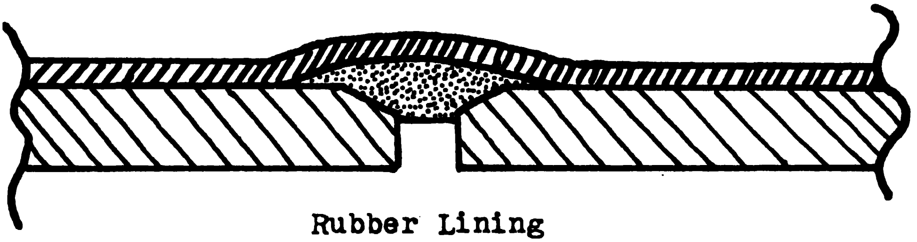
FIG. XIX–9.—LINED TANK ENTERING VULCANISING PAN.
Pan size 15 ft. dia. × 20 ft. long.

(Courtesy of Dunlop Rubber Co.)

advice should be sought previously. Coverings of hard ebonite can be used at 100°–120°, but soften notably at all temperatures above 70°. If, however, the ebonite is backed by steel, to which adhesion is very good, this loss of rigidity is not serious, and vulcanite-covered centrifugal pumps have been used for hot hydrochloric acid solutions. There are few limits to the size or complexity of plant sections that can be covered by rubber, from the racks of Fig. XIX–11, to the tanks shown in Fig. XIX–12, and the fan of Fig. XIX–13, which shows how complete is resistance to centrifugal stress. A rubber lining is now (1953) being fitted to a 24-million-gallon reservoir, which has cracked through subsoil subsidence.



Rubber Lining
on Unprotected Seam



Rubber Lining
on Seam Protected with Rubber Cement

FIG. XIX–10.

The various synthetic rubbers have been used in the same way as the natural article, but have not given such satisfaction, at any rate for linings. Adhesion to metals is not, so far, as good as with vulcanised rubber, but this may merely be lack of experience in handling. Butyl rubber is fairly resistant to vegetable fats and fatty oils, and also relatively impervious to gases. When a rubber-lined tank is required to operate at 100° for long periods, a butyl rubber lining may give better service than natural rubber. Neoprene is essentially oil-resistant, though not recommended for storage of solvents. Other forms have not found any extensive application in the chemical field, where cost stands in the way of wider adoption. All synthetic rubbers, at any rate in this country, cost from two to three times as much as the natural product, though relative figures are more than usually unstable. The price of raw rubber has varied from 2*d.* up to 6*s.* per pound—a thirty-fold variation and more—over the last twenty years.

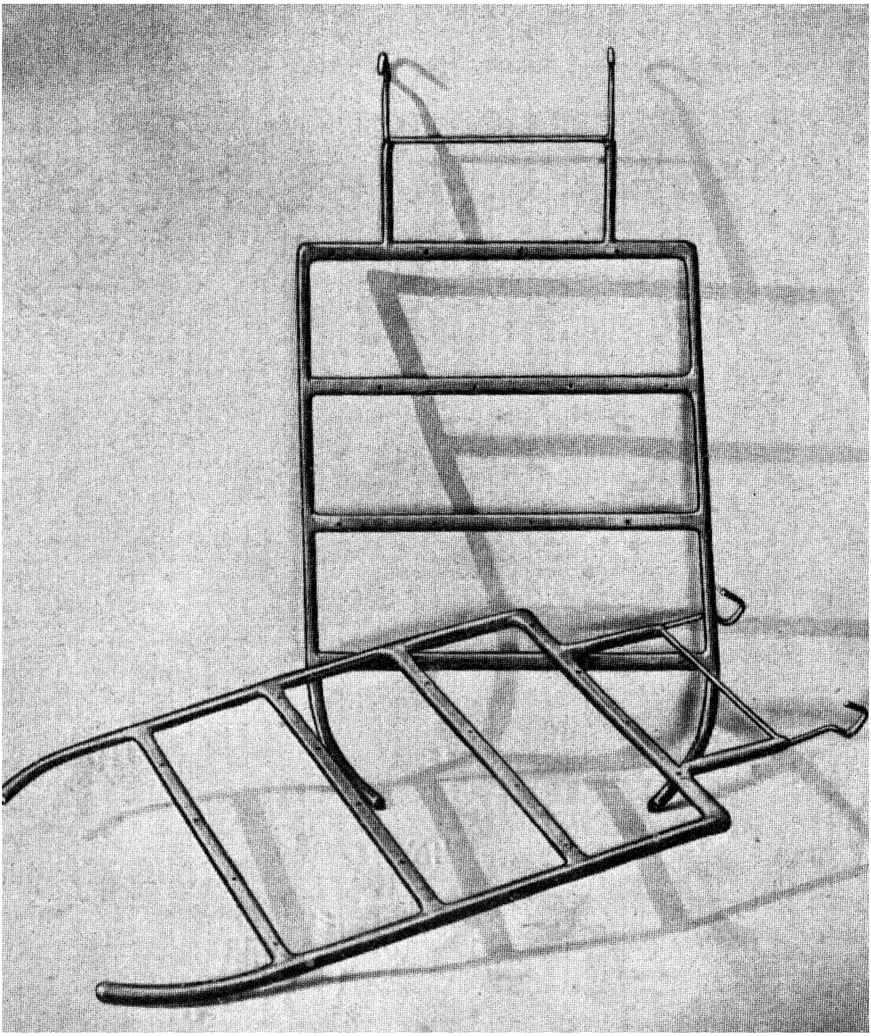


FIG. XIX-11.—RUBBER-COVERED RACKS.

(Courtesy of Andre Rubber Co.)

Corrosion Resistance

Non-oxidising acids, such as hydrochloric (all strengths) and sulphuric (up to 50%), have no appreciable action on hard vulcanite, filled rubber, or "pure" rubber within the proper working temperatures. Sulphurous acid can slowly attack the softer rubber mixes, and a special filling, or hard vulcanising, is desirable. Nitric acid should not be in contact with any form of rubber. All normal plating solutions, containing heavy and precious metals, can be handled in rubber-lined tanks or pumped with rubber pumps. A special glandless pump, based on the peculiar mechanical properties of rubber, is shown in Fig. XIX–14, and was designed[14] for handling hot concentrated solutions of iron in hydrochloric acid. Very strong hydrochloric acid solutions have a hardening effect on pure rubber when used at boiling-point, and ebonite is preferable. Phosphoric acid can be handled at any concentration if the temperature

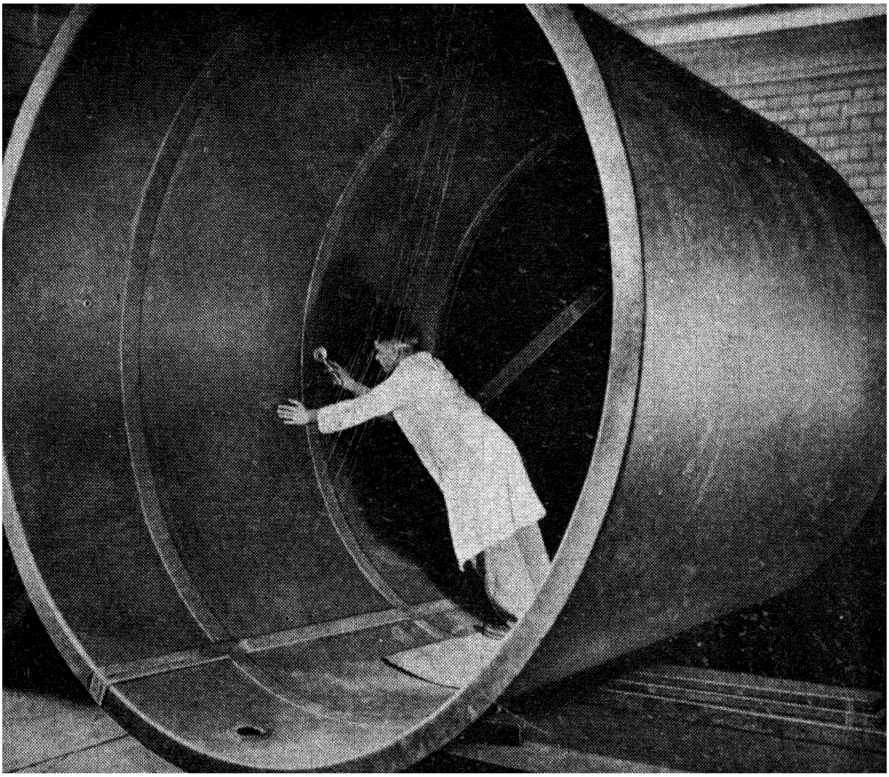


FIG. XIX–12.—RUBBER-LINED TANK.
(*Courtesy of Andre Rubber Co.*)

is below 50°, and a rubber-lined ball-mill has been used successfully in grinding phosphate rock with sulphuric acid (30%) to make phosphoric acid. The free halogens all attack rubber, but a hard

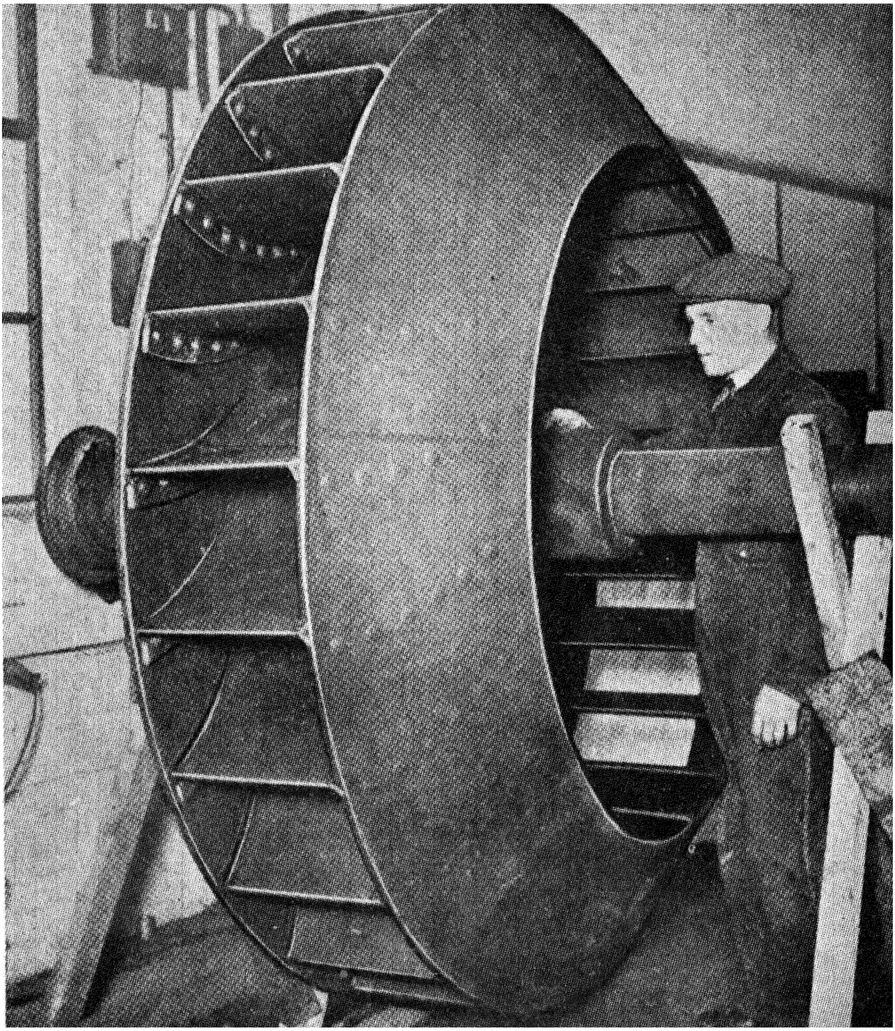


FIG. XIX-13.—RUBBER-LINED FAN—7 FT. DIAMETER.
(*Courtesy of Nordac, Ltd.*)

addition product forms over the surface and checks further reaction. Ebonite plant has been used successfully for aqueous chlorine solutions, and cold sodium hypochlorite is often stored in rubber-lined tanks, serviced by ebonite valves (Fig. XIX-15).

Neutral, or slightly alkaline, salt solutions at temperatures up to 90° are quite unaffected by either hard or soft rubber, and freedom from metallic contamination makes it possible to produce colourless crystals in a rubber-lined plant. Crystallisation processes have always suffered from the fact that the growing crystals stick to the sides of the vessel and deform, or have to be chipped away at intervals. The adhesion is an indication of incipient reaction, and the inert rubber surface offers no lodgment for the crystal nucleus. The modern form of vacuum crystalliser suspends a mass of growing crystals in a rapidly moving liquid mass, and the effects of abrasion are negligible on a rubber surface, though steel may suffer.

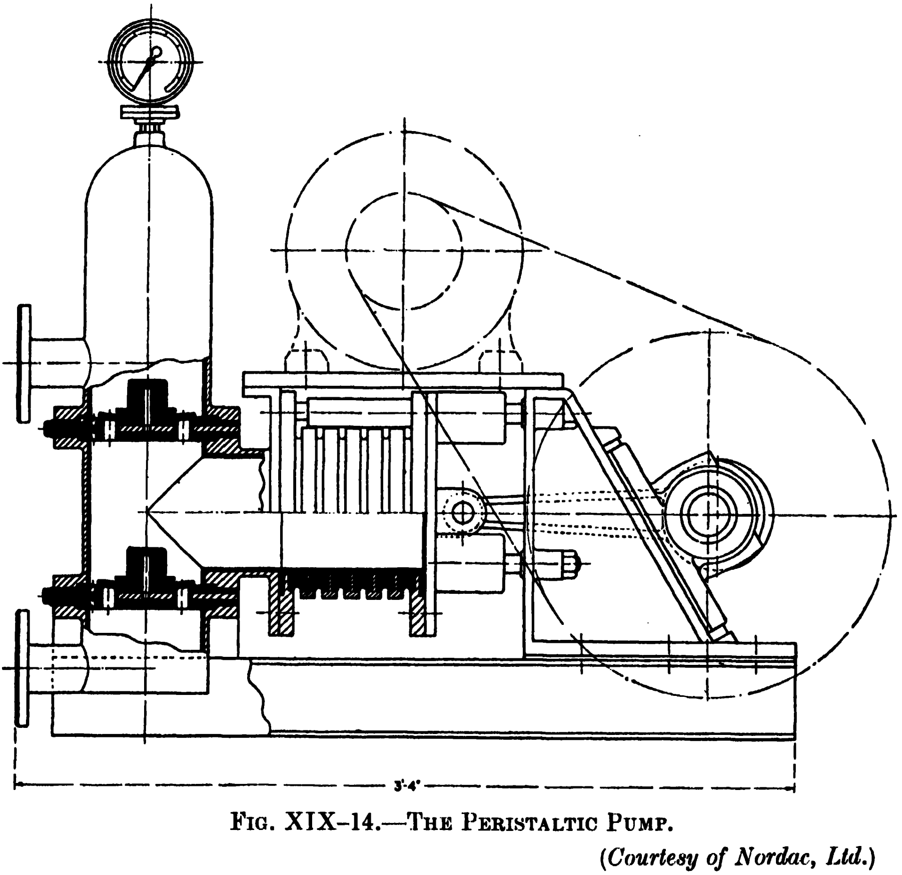


FIG. XIX-14.—THE PERISTALTIC PUMP.

(*Courtesy of Nordac, Ltd.*)

It is unusual to put any organic liquids into rubber containers as there are many obvious alternatives, but many oils and solvents do not attack even soft rubber, and still less the more stable vulcanite. These are polar liquids of the type of alcohols, acids, and the simpler ketones, while aqueous solutions of amines or organic acids are quite innocuous. Foodstuffs, fruit juices, soaps, and gelatines, in which metallic contamination must be avoided, have been manufactured and stored in rubber-lined plant. If some organic constituent is to be mixed in circumstances which suggest the use of rubber, then the synthetic butyl or neoprene substitutes should be considered.[15]

The silicone-based rubber-like materials are still in the experimental stage and are very expensive. The principal advantage that may be offered over all other forms is temperature resistance. "Silastic", one proprietary form of silicone rubber, has been prepared in various grades, some of which will retain full elasticity from —50° to +250° C. Carbon black is no use as a filler, and various metallic oxides or some form of silica are used. When properly chosen, resistance to chemicals is better than most, if not all, elastomeric substances. All dilute aqueous solutions, acid and basic alike, have little effect, while some "Silastics" resist concentrated nitric acid or 50% caustic soda solution.[16] It is still true that aromatic hydrocarbons and chlorinated solvents swell and weaken the rubber, but the action is much less marked than with other synthetic products, and a paraffinic oil has no appreciable action. Resistance to weather—air and sunlight—is particularly good. It may well be that this material has a very definite future in chemical plant work, but the product is still in the early stages of development.

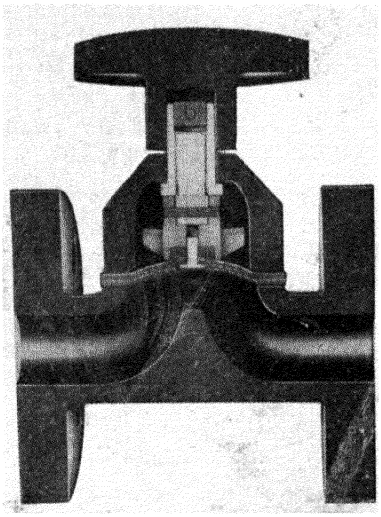


FIG. XIX-15.—VALVE IN EBONITE (with Soft Rubber Diaphragm).
(*Courtesy Dexine Rubber and Ebonite, Ltd.*)

REFERENCES

Seymour, R. B., and Steiner, R. H., *Chem. Eng.*, 1952, **59** (Dec.), p. 278.
2. B.S. 668, 1137, etc.
3. Registered Trade Name, Kestner Evaporator and Eng. Co.
4. Black, G. H., *Chem. and Ind.*, 1952, 727.
5. Fisher, C., *Chem. Process Eng.*, 1953, **34**, 5.
6. Zamzow, W. H., and Marshall, W. R., *Chem. Engng. Progr.*, 1952, **48**, 21.
7. *British Plastics*, 1951, **24** (May), p. 150.
8. *Industrial Chemist*, 1952, **28**, 511.
9. Jaray, F. F., "Materials of Construction", p. 199.
10. *Chem. Eng.*, 1952, **59** (Mar.), p. 138; Stanley, T. A., "Materials of Construction," p. 227.
11. See also Bachman, G. B., *et al.*, *Ind. Eng. Chem.*, 1951, **43**, 997; Fisher, H. L., *Ind. Eng. Chem.*, 1951, **43**, 2227.
12. Stevens, H. P., and Donald, M. B., "Rubber in Chemical Engineering", Rubber Development Board, 1951.
13. Swindin, N., "Materials of Construction", p. 211.
14. Swindin, N., *Proc. Chem. Eng. Grp.*, 1944, **26**, 56.
15. Brazier, S. A., *Trans. Inst. Chem. Eng.*, 1952, **30**, 46.
16. Bass, S. L., *Proc. 2nd Rubber Tech. Conf.*, Inst. Rubber Ind., 1948, p. 17.
17. Anon., *Chem. Proc. Eng.*, 1953, **34**, 149.
18. G. S. Laaff, *Chem. Eng.*, 1953, **60** (June), 312.
19. B. S. 1972, 1973.
20. As (18), above.
21. Makers Claim—"Ferobestos LA4"—Ferodo Ltd.
22. Bruner, W. M., and Wayne, P. J., *Chem. Eng.*, 1953, **60**, 193.
23. But see Evans, V., *Chem. Proc. Eng.*, 1953, **34**, 307.
24. Seymour, R. B., and Erich, E. A., *Chem. Engng. Progr.*, 1952, **48**, 374.

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